

R. W. Conant
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Elementary Photographic Chemistry

Eastman Kodak Company
Rochester, N. Y.



So very, very
true, and so
very, very
pretty.

Just as
pictured.

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Eastman Kodak Company

Rochester, N. Y.

1928

INTRODUCTION

Photography is so essentially a chemical process that every photographer should have an interest in the chemicals which he uses and in the reactions which they undergo.

This book is written in response to a demand for a simple account of photographic chemistry, for the practical photographer.

No attempt has been made to give the chemical theory in full, for which textbooks on chemistry should be consulted. In Chapter I, a statement is given only of the chemistry which is necessary to an understanding of the remainder of the book. In the same way reference should be made to photographic textbooks for general photographic practice.

To give the information about photographic chemicals which is necessary for their intelligent use, the properties of each of the more important chemicals are given in a separate paragraph, which is inserted in the section dealing with its use, in a distinct type face to facilitate reference. A table of solubilities of the chemicals in common photographic use is given at the end of the book. Practical information on formulas, preparing and using photographic solutions is given in Chapters VIII, IX and X.

No apology is necessary for the insistence placed on the need for pure chemicals and on the advantage to be gained by using the Eastman Tested Chemicals, which are specially purified and tested for photographic use.

EASTMAN KODAK COMPANY,
ROCHESTER, N. Y.

October, 1928.

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CHAPTER I.

An Outline of Elementary Chemistry

All substances are made by the combination in various proportions of a limited number of *elements*, of which about ninety exist. These elements combine in definite proportions to form bodies of fixed composition, which are termed *compounds*. Thus, one volume of the gaseous element hydrogen combines with one volume of the gaseous element chlorine to form two volumes of the compound hydrochloric acid gas. This combination can be represented by what is called a chemical equation. If we write *H* for hydrogen, *Cl* for chlorine and *HCl* for hydrochloric acid, we can represent the above combination by the equation



It will be seen that an equation such as that given above is really a shorthand method of stating what happens, the elements which take part in the combination being designated by letters. These letters which stand for the elements are called the "symbols" of the elements.

The elements which are of the greatest importance in photography and their symbols are as follows:

Gases

Name	Symbol	Remarks
Hydrogen	H	The lightest gas known.
Nitrogen	N	Forms 80% of the air. (Approx.)
Oxygen	O	Forms 20% of the air. (Approx.)
Chlorine	Cl	Greenish-yellow poisonous gas.
Bromine	Br	Poisonous brownish-red gas at high temperatures, liquid at ordinary temperatures.

Non-metallic Solids

Name	Symbol	Remarks
Carbon	C	Occurs in three forms: diamond, graphite, and charcoal or amorphous carbon.
Sulphur	S	Yellowish-white, brittle solid.
Iodine	I	Violet plate-like crystals, similar in chemical properties to chlorine and bromine.

Metallic Solids

Name	Symbol	Remarks
Sodium	Na	Very light, attacked by moisture, kept under light oil.
Potassium	K	Very light, attacked by moisture, kept under light oil.
Calcium	Ca	Silvery white metal, attacked by moisture.
Aluminum	Al	Very light, white metal.
Iron	Fe	In the pure state it is called wrought-iron; when containing a small amount of carbon it forms cast-iron and steel.
Copper	Cu	Reddish, tough metal.
Silver	Ag	White metal.
Platinum	Pt	Valuable white metal, very heavy.
Gold	Au	Reddish yellow metal, very heavy.
Mercury	Hg	White metallic liquid, very heavy.

These elements fall into two groups; those which are metals and those which are not metals. Apart from the appearance of the elements, the classification of an element in one of these two groups depends upon its relation to oxygen. Many of the elements when heated in the presence of oxygen will combine with it and will form what are called *oxides*. Thus, carbon will burn in oxygen and will form a gaseous compound of carbon with oxygen called *carbon dioxide*. Iron will burn in oxygen and forms a solid iron oxide.

Oxides of Elements

Name	Symbol	Remarks
Hydrogen oxide (water)	H ₂ O	Can be made by burning hydrogen in air or oxygen.

Acid Oxides

Carbon dioxide	CO ₂	A heavy gas, is produced by burning carbon; e.g., charcoal.
Nitric oxide	NO	Colorless gas, turns reddish-brown in contact with oxygen.
Sulphur dioxide	SO ₂	Colorless gas. Produced by burning sulphur.

Basic Oxides

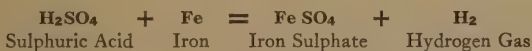
Aluminum oxide	Al ₂ O ₃	White powder formed when aluminum is burned in the air.
Calcium oxide	CaO	Quicklime, obtained by heating chalk.
Iron oxide	Fe ₂ O ₃	Red powder formed when iron rusts.
Mercuric oxide	HgO	Red powder formed by slow heating of mercury in the air.

Many oxides are soluble in water, forming two classes of compounds, which are known respectively as *acids* and *bases*, the acid oxides being produced from the non-metallic elements and the basic oxides from the metallic elements. Thus, carbon, nitrogen and sulphur all form acid oxides which dissolve in water to form acids, while sodium, potassium and calcium form typical basic oxides which dissolve in water to form bases.

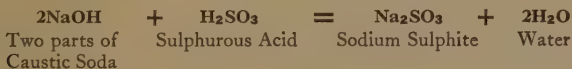
Bases are either alkaline or earthy, the alkaline bases being soluble, the earthy bases insoluble. The ordinary way of distinguishing between an acid and a base is to test the solution with a trace of certain dyes which change color according to whether the solution is acid or alkaline. Thus, if a piece of paper soaked in a solution of litmus, generally known as litmus paper, is put into a solution, it will turn red if the solution is acid, and blue if the solution is alkaline. Sodium forms an oxide which dissolves in water and makes a solution of basic caustic soda, the caustic soda having the formula NaOH , and being composed of sodium, oxygen and hydrogen. On the other hand, sulphur combines with oxygen and the oxide dissolves in water to form sulphurous acid, this having the formula H_2SO_3 and being formed by the combination of water, H_2O , with sulphur dioxide, SO_2 . Thus:



All acids contain hydrogen and this hydrogen can be replaced by a metal, forming a compound which is termed a "salt." Thus, if we have sulphuric acid and we dissolve a piece of iron in it, the iron will replace the hydrogen of the acid, which will be given off as bubbles of gas and a solution of the salt, iron sulphate, will be formed:



Salts are also formed by the direct union of an acid and a base. Thus, if we have caustic soda, NaOH , and sulphurous acid, H_2SO_3 , they combine to form sodium sulphite, eliminating water. Thus:



It will be seen that the sodium sulphite is formed by the combination of the base derived from sodium with the acid derived from sulphur.

Sometimes a non-metallic element forms two different oxides, and these in turn will form two different acids. When we burn sulphur in oxygen, for instance, each atom of sulphur combines with two atoms of oxygen and forms sulphur dioxide:



and this dissolves in water to form sulphurous acid. If the sulphur dioxide is passed, with more oxygen over heated platinum, it is possible to make it combine with another atom of oxygen and form the compound sulphur trioxide, SO_3 , and this dissolves in water and forms sulphuric acid:



so that from sulphur we not only get sulphurous acid but a second acid—sulphuric acid.

Just as the hydrogen of sulphurous acid is replaced by sodium to form sodium sulphite, so the hydrogen of sulphuric acid is replaced by sodium to form sodium sulphate.

Sulphur Dioxide	SO_2	Sulphur Trioxide	SO_3
Sulphurous Acid	H_2SO_3	Sulphuric Acid	H_2SO_4
Sodium Sulphite	Na_2SO_3	Sodium Sulphate	Na_2SO_4

Salts are usually neutral to litmus paper, though sometimes they are somewhat acid or alkaline. But in addition to the neutral salts, an acid in which there are two hydrogen atoms can have one of them replaced by a metal instead of both, and in this case we get acid salts, which are equivalent in their behavior to a mixture of equal parts of the acid and the neutral salt. For instance, from sulphurous acid if we replace both the hydrogens, we get sodium sulphite— Na_2SO_3 —but if we replace only one of the hydrogens, we get the compound $NaHSO_3$, which is called sodium acid sulphite, sodium hydrogen sulphite or, more usually, sodium bisulphite.

Sulphur forms a number of different acids. It forms not only acids from its two oxides SO_2 and SO_3 , but it forms compound acids containing more than one atom of sulphur, and of these, one is of very great importance to the photographer, namely, thiosulphuric acid, which forms a sodium salt, sodium

thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$. It will be seen that this compound differs from sodium sulphite in having two atoms of sulphur instead of one, and it is the compound, generally known as "hypo," which is used for fixing photographic materials.

Some acids are formed not from oxides but by the direct combination of a non-metallic element with hydrogen, and of these the most important are the strong acids formed from chlorine, bromine and iodine, which three elements, because they occur in sea salt, are called halogens, from the Greek words, salt producing. Thus, chlorine combines directly with hydrogen to form hydrochloric acid, H Cl , and if the hydrogen of this is replaced by metals, we get chlorides, of which the best known is sodium chloride, Na Cl , which is common salt. Similarly, bromine combines with hydrogen to form hydrobromic acid, with which metals form bromides, and in the same way the iodides are formed from iodine.

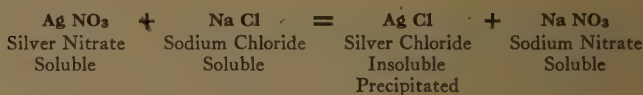
The Halogens, Their Acids and Salts

Halogen Element	Acid	Sodium Salt
Cl Chlorine	HCl Hydrochloric Acid	NaCl Sodium Chloride
Br Bromine	HBr Hydrobromic Acid	NaBr Sodium Bromide
I Iodine	HI Hydriodic Acid	NaI Sodium Iodide

Salts are soluble in water to different extents, the solubility depending upon the nature of the salt. Some, such as hypo, are extremely soluble, hypo being soluble in less than its own volume of water; while others are only slightly soluble or even almost completely insoluble, silver chloride, bromide and iodide being well known examples of very insoluble materials. A solution of a salt may be regarded as containing both the basic and the acid components of the salt in a more or less free condition. For instance, all copper salts in solution behave in much the same way, showing properties in common, due to the presence of the copper. In the same way all chlorides or sulphates show common properties in solution.

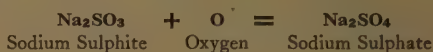
Now, when we mix two solutions of soluble salts, and the base of one can form an insoluble salt with the acid of the other, then this rearrangement will take place and the insoluble substance will be thrown out of solution as a precipitate. Thus, silver nitrate and sodium chloride are both very soluble in water, but when the solutions are mixed, the silver and the sodium change places so that silver chloride and sodium nitrate are formed, and the almost insoluble silver

chloride is thrown out of the solution, leaving only the sodium nitrate behind.



This "double decomposition" is the simplest kind of chemical reaction and is the one with which we are most familiar.

Other types of chemical reaction which are of great importance in photography are those of oxidation and reduction. The simplest example of oxidation is, of course, that in which an element combines with oxygen; but when an element forms two or more compounds with oxygen, then we are said to perform oxidation when we raise the element from the level of oxidation of one of its compounds to another level in which it is combined with more oxygen. For example, by the oxidation of sodium sulphite, Na_2SO_3 , which is a compound formed from sulphur dioxide, SO_2 , we get sodium sulphate Na_2SO_4 , which is derived from sulphur trioxide, SO_3 . This can be done by means of oxygen. If we pass air, which contains 20% of oxygen (the rest being chiefly nitrogen), through a sulphite solution, or even leave sodium sulphite exposed to the air for long periods, it will be oxidized into sulphate—



When metallic elements form two oxides with different amounts of oxygen, these two oxides will act as bases for two series of salts. Thus, iron forms

Ferrous salts derived from Fe O , and

Ferric salts derived from Fe_2O_3 .

Thus, we have

Ferrous Chloride, Fe Cl_2 , green crystals,

Ferric Chloride, Fe Cl_3 , red-brown crystals.

Very often oxidation is accomplished not by the use of oxygen itself but by the use of some substance which itself is a higher compound of oxygen and which can be reduced to a lower compound of oxygen or to an element which contains no oxygen at all. Thus, for instance, when hydroquinone is oxidized, we get quinone, which we call the oxidation product of hydroquinone, but if we add sulphite to quinone, the quinone oxidizes the sulphite to sulphate and is itself reduced

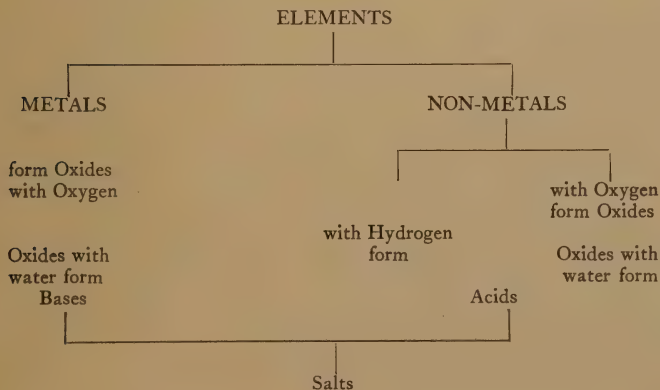
again to hydroquinone. In this case the sulphite acts as a *reducing* agent, reduction being the opposite to oxidation. Thus, a body which is easily oxidized will take the oxygen it needs from other substances and so acts as a reducing agent. *Hydroquinone* is oxidized to *quinone*, which is reduced by sulphite to *hydroquinone*. Conversely, the *sulphite* is oxidized by the quinone to *sulphate*.

Similarly, if we add *ferric* salts to hydroquinone, they will oxidize it to *quinone* and will themselves be reduced to *ferrous* salts.

The term reduction is applied especially to the liberation of metallic elements from their compounds. If we heat mercuric oxide, the oxygen is driven off by the heat and the mercuric oxide is reduced to mercury. Generally, reduction cannot be accomplished by heat alone, and it is necessary to have some substance present which can be oxidized in order to reduce a compound. Thus, to reduce iron from its oxide, of which iron ore is chiefly composed, we heat it with charcoal or carbon, which is oxidized to form carbon dioxide and which reduces the iron oxide to metallic iron.

Chemical compounds consist of five great classes:

1. **ACIDS**, which are formed from non-metallic elements and which contain hydrogen replaceable by a metal;
2. **BASES**, which are formed from the metallic elements, and which, when soluble in water, are called alkalis;
3. **SALTS**, which are formed from the combination of an acid and a base;
4. **OXIDIZERS**, which are substances containing an excess of oxygen and which can give up this oxygen to another compound;
5. **REDUCERS**, which are greedy for oxygen and which take the oxygen away from any compound containing an available supply of it.



CHAPTER II.

The Chemistry of Photographic Materials

The art of photography is founded upon the fact that the compounds of silver, and especially its compounds with chlorine, bromine and iodine, are sensitive to light.

The earliest photographs were made by coating paper with silver chloride and using this to form images by its darkening under the action of light, but the sensitiveness of the silver chloride was too slight to use it in this way to form images in the camera.

To get results which require less exposure to light, advantage is taken of the fact that it is not necessary for the light to do the whole work of forming the image; it is possible to expose the silver salt for only a short time to the light and then to continue the production of the image by chemical action, the process being termed "development."

Sensitive photographic materials therefore consist of paper, film, or glass coated with a layer in which is suspended the sensitive silver bromide or silver chloride. This layer is called the *emulsion*. This emulsion consists of a suspension of the silver salt in a solution of gelatin. It is made by soaking gelatin in water until it is swollen and then dissolving it by gently warming and stirring. The necessary bromide or chloride, e.g., potassium bromide or sodium chloride, is then added to the solution and dissolves in it. Meanwhile, the right quantity of silver nitrate to react with the quantity of salts used has been weighed out and is dissolved in water. The silver nitrate solution is then added slowly to the solution of gelatin and salt and produces in it a precipitate of the silver compound, the mixing being done in the darkroom, since the silver compound produced is sensitive to light. If there were no gelatin in the solution the silver compound would settle down to the bottom and an emulsion would not be formed, but the gelatin prevents the settling so that as the silver nitrate is added a little at a time, the precipitated silver salt is uniformly distributed through the solution. If this emulsion is coated on a support, such as paper or film and

then cooled, the gelatin will set to a jelly, and when the jelly is dried we get a smooth coating of dry emulsion of the sensitive silver compound.

Photographic materials which are to be developed must contain no excess of soluble silver and the emulsion must be made so that there is always an excess of bromide or chloride, since any excess of soluble silver will produce a heavy fog over the whole of the surface as soon as the material is placed in the developer. In the case of Solio paper, however, which is not used for development but which is printed out, a chloride emulsion is made with an excess of silver nitrate. This causes rapid darkening in the light, so that prints made upon Solio paper are not developed, the visible image being toned and fixed. Solio paper can be developed with certain precautions, such as by the use of acid developers or after treatment with bromide to remove the excess of silver nitrate.

In the early days of photography prints were usually made on printing-out papers, but at the present time most prints are made by the use of developing-out chloride and bromide papers, which are chemically of the same nature as the negative making materials and are coated with emulsions containing no free silver nitrate.

Negative making materials such as plates and films, always contain silver bromide with a small addition of silver iodide. The different degrees of sensitiveness are obtained by varying the temperature and the duration of heating which the emulsions undergo during manufacture, the most sensitive emulsions being heated to higher temperatures and for a longer time than the slower emulsions.

If a slow bromide emulsion is coated upon paper, the material is known as *bromide paper* and is used for printing, and especially for making enlargements. The less sensitive papers which are commonly used for contact printing by artificial light contain silver chloride in the place of silver bromide.

In order to obtain silver nitrate the first step is to dissolve metallic silver in nitric acid. The silver replaces the hydrogen of the acid and forms silver nitrate, the hydrogen liberated decomposing a further portion of the nitric acid. The silver nitrate is crystallized out of the solution and obtained in colorless, transparent plates.

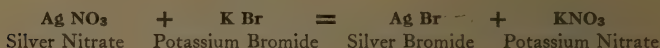
SILVER NITRATE for photographic use has to be extremely pure, and since metallic silver usually contains a small quantity of other metals, such as copper and lead, it is necessary to free it from these impurities. This is

accomplished by recrystallization, so that the silver nitrate is finally obtained in a perfectly pure form.

In order to insure the purity of the silver nitrate which it uses, the Eastman Kodak Company prepares its own and is the largest maker of silver nitrate in the world, using about one-eleventh of all the silver mined in the United States, the Mint only, using more.

Silver nitrate is very soluble in water. It attacks organic material, and blackens skin, wood, cloth, and other similar substances on exposure to light.

When a solution of silver nitrate is added to a solution of a bromide or chloride of another element, a reaction occurs and the insoluble silver bromide or chloride is precipitated. Thus, if we add silver nitrate to potassium bromide, the reaction occurs according to the following equation:



The potassium nitrate formed remains in solution, but if the solution is at all concentrated, the silver bromide is thrown down to the bottom of the vessel as a thick, curdy precipitate.

The bromides and chlorides used in photography are chiefly the salts of potassium and sodium. Both the bromides and the chlorides are obtained from naturally occurring salt deposits, but, whereas these deposits consist chiefly of chlorides, they contain only a very small quantity of bromide, and bromide is therefore a very much more expensive material than chloride.

The elements chlorine, bromine and iodine are all obtained from natural salt or from the sea, iodine being derived from certain sea weeds which extract it from the sea water and thus make it available in a concentrated form. Chlorine is a yellowish-green gas, very suffocating and poisonous, bromine gives dark red fumes which are even more noxious than chlorine and condense to a liquid, and iodine forms shining, black crystalline flakes which on heating give a violet vapor. The chief chlorides, bromides and iodides used in photography are the following:

AMMONIUM CHLORIDE: White crystals soluble in water. Made from ammonia and hydrochloric acid, should have no smell, and when evaporated by heat should leave no residue behind.

AMMONIUM BROMIDE: Very similar to the chloride, which is the only impurity likely to be present.

AMMONIUM IODIDE: Should consist of colorless crystals. Decomposes in light and is stained yellow by the iodine liberated. Very soluble in water and deliquescent (see p. 23). Soluble in alcohol.

SODIUM CHLORIDE: Ordinary table salt is fairly pure sodium chloride and a very pure salt is easily obtained. The pure salt is stable and not deliquescent. Soluble in cold water (40°F.) (4°C.) to the extent of 31 ounces of salt to 100 fluid ounces of solution. Solubility increases very little on heating.

SODIUM BROMIDE: A white salt, similar to the chloride but more soluble. Is generally pure but may contain chloride.

POTASSIUM CHLORIDE: White salt, very similar to sodium chloride.

POTASSIUM BROMIDE: Occurs as colorless cubical crystals and is generally pure. To facilitate handling and weighing potassium bromide is usually supplied in the granular form. Very soluble in water.

POTASSIUM IODIDE: Similar to bromide. Very soluble. May contain as impurities carbonate, sulphate and iodate, but is usually pure. A solution of potassium iodide dissolves iodine, which is insoluble in water, and it is therefore used to prepare a solution of iodine.

The gelatin which is used to emulsify the sensitive silver salts is a very complex substance which is obtained from the bones and skins of animals. Gelatin has some curious and valuable properties. In cold water it does not dissolve but it swells as if, instead of the gelatin dissolving in the water, the water dissolves in the gelatin. If the water is heated, the gelatin will dissolve, and it can be dissolved to any extent. It cannot be said that there is a definite solubility of gelatin in water in the same sense as salts may be considered to have a definite solubility. As more gelatin is added, the solution becomes thicker. If the gelatin solution is heated, it will become thinner and less viscous when hot, and will thicken again as it cools, but it will remain thinner than if it had not been heated, so that the heating of the gelatin solution produces a permanent change in its properties. If a gelatin solution is cooled, the gelatin will not separate from the solution in a dry state but the whole solution will set to a jelly. If the jelly is heated again, it will melt, and a jelly can be melted and reset many times. During the treatment there will be produced a progressive change in the jelly, and if the process is continued long enough, the solution will refuse to set and will remain as a thick liquid.

Gelatin belongs to the class of substances which are called colloids, the name being derived from a Greek word meaning "gummy." When a gelatin jelly is dried it shrinks and forms a horny or glassy layer of the gelatin itself, smooth and rather brittle. This dry gelatin, when placed in water, will at once absorb the water and swell up again to form a jelly. This swelling and shrinking are of great importance in photog-

raphy. When a photographic material with an emulsion made with gelatin is placed in water, the film will swell up and will continue to absorb more water and swell for a long time, finally becoming soft and even dissolving, the extent to which this occurs depending on the temperature and the nature of the solutions in which it is placed. A small quantity of either an acid or alkali will produce a considerable increase in the swelling, and since the developer is alkaline and the fixing bath is acid, both these solutions have a great tendency to swell the gelatin, especially when they are warm. In order to avoid difficulty from this source, gelatin emulsions have a hardener added before they are coated, gelatin being hardened and made more resistant to swelling by the addition of alum.

Under ordinary circumstances no difficulty is experienced by the photographer due to the softening of the gelatin, but when photographic materials are exposed to extreme temperatures, care must be taken in handling them. Hardening agents such as alum must be added to the fixing bath, and all solutions must be kept at the same temperature in order to avoid sudden contractions or expansions of the gelatin which may result in detaching the film from its support or in the production of reticulation, i.e., a coarse wrinkling all over the film.

CHAPTER III.

The Chemistry of Development

When a light sensitive material is exposed for a short time to light, although the change which takes place may be so minute that it cannot be detected by any ordinary means, if the exposed material is placed in a chemical solution, which is termed the "developer," the chlorine or bromine is taken away from the silver, and the black metallic silver which remains behind forms the image. This image is, of course, made up of grains, because the original emulsion contains the silver bromide in the form of microscopic crystals, and when the bromide is taken away from each of these, the crystal breaks up and a tiny coke-like mass of metallic silver remains behind in exactly the same position as the bromide crystal from which it was formed, so that, whereas the original emulsion consisted of microscopic crystalline grains of the sensitive silver salt, the final image consists of equally microscopic grains of black metallic silver. This removal of the bromide from the metallic silver is known chemically as *reduction*. (It must be remembered that chemical reduction has nothing to do with the photographic operation known as the reducing of a negative; that is, the weakening of an over-dense negative, where the word simply refers to the removal of the silver and is not used in the chemical sense.)

Chemical reducers are substances which have an affinity for oxygen and which can liberate the metals from their salts, such as the charcoal which, as explained in Chapter I, is used to reduce iron from its ore. A developing solution is therefore one which contains a chemical reducer. All substances which are easily oxidized are, however, not developers, since in order that a reducer may be used as the photographic developer it is necessary that it should be able to reduce exposed silver bromide but should not affect unexposed silver bromide, so that its affinity for oxygen must be within certain narrow bounds; it must be a sufficiently strong reducer to reduce the exposed silver salt, and at the same time must not affect that which has not been exposed. For practical purposes the developing agents are limited to a very few substances, almost all of which are chemically derived from benzene, the light oil which is distilled from coal tar.

The commonest developing agents are pyrogallol (pyro), hydroquinone, Elon, para-aminophenol or Kodelon, and diaminophenol.

PYROGALLOL (or pyrogallic acid) is made from gallic acid, which is obtained from gall nuts imported from China. The gall nuts are fermented to obtain the gallic acid, and the gallic acid is then heated in a still from which the pyrogallol is distilled over. Pyrogallol is made in two forms: a flaky powder form and a crystal form. When the powdered pyrogallol is opened in the darkroom or studio, the fine particles fly about and are likely to settle on paper or plates, producing spots on the photographs. For this reason the Eastman Kodak Company manufactures and supplies pyrogallol in the crystal form, which can be handled without any danger of particles flying about and giving trouble.

HYDROQUINONE is made from benzene which is first converted into aniline and then oxidized. Although it is somewhat less powerful as a reducing agent than pyro, it has less propensity to give stain and when used in conjunction with Elon or Kodelon it is a very useful developer, in fact, it is a constituent of a majority of the better known commercial developers in use today. It keeps very well when used in tank developers because it does not oxidize as readily as pyro and is generally used in motion picture work. Its purity is very important and Eastman Tested Hydroquinone, manufactured by the Company, may be relied upon for all formulas.

Some time after pyrogallic acid and hydroquinone were in general use by photographers, there were introduced a number of new developing agents made from coal tar, which are very useful as supplements to the older developers. Several of these are based on a substance called *para-aminophenol*, which is made in the manufacture of dyes. When para-aminophenol is treated with methyl alcohol the methyl part of the alcohol attaches itself to it and forms a compound called *methyl-para-aminophenol*, which is a more active developing agent than the para-aminophenol itself. Another developing agent of the same type is *diaminophenol*, which is prepared in a way similar to para-aminophenol.

Para-aminophenol, methyl-para-aminophenol and diaminophenol are all bases and the developing agents are their salts, the oxalate of para-aminophenol, the hydrochloride of diaminophenol being used, and the sulphate of methyl-para-aminophenol.

Para-AMINOPHENOL OXALATE is manufactured and sold by the Eastman Kodak Company under the name of *Kodelon*. Many of the so-called "new" developing agents on the market consist entirely or mainly of para-aminophenol. A good sample should be light in color and should burn entirely when heated to redness, leaving no ash behind.

MONOMETHYL Para-AMINOPHENOL SULPHATE manufactured and sold by the Eastman Kodak Company under the name of *Elon*. Mono-

methyl para-aminophenol sulphate is distinguished sharply from para-aminophenol oxalate by the fact that it is soluble in the cold in its own weight of strong hydrochloric acid, whereas the para-aminophenol oxalate is insoluble.

DIAMINOPHENOL HYDROCHLORIDE is sold by the Eastman Kodak Company under the trade name of *Acrol*. It is a steel gray powder, darkening easily in the air and is oxidized so rapidly in solution that it is usual to dissolve it only when required for use.

Different reducing agents behave differently as developers. We cannot use Elon in the place of hydroquinone and get the same effect. An image developed with Elon comes up very quickly and gains density slowly, while the hydroquinone image comes up very slowly but gains density steadily and rapidly. A very little change in the temperature affects hydroquinone greatly and affects Elon very little, and in the same way a small quantity of sodium or potassium bromide affects hydroquinone and does not affect Elon nearly so much. These differences in the developing agents depend upon the chemical nature of the substances themselves, and the particular property to which these differences are due is called the "reduction potential" of the developer.

The reduction potential alone does not determine the speed with which the developer develops the image, because this depends chiefly upon the rate at which the developer diffuses into the film and on the quantity of developing agent and other substances in the developer. A high reduction potential enables a developer to continue to develop more nearly at a normal rate under adverse circumstances, such as at a low temperature or in the presence of bromide. The reduction potential of a developer, in fact, may be compared to the horse-power of an automobile which for other reasons than the power of its engine is limited in speed. If we have two automobiles and they are confined to a maximum speed of twenty miles an hour, then on level roads the one with the more powerful engine may be no faster than that with a weaker engine, but in a high wind or on a more hilly road the more powerful engine will allow the automobile to keep its speed, while the machine with the weaker engine will be forced to go more slowly. We could, indeed, measure the horse-power of an automobile by the maximum grade which it could climb at a uniform speed of 20 miles an hour.

In development, the analogy to the hill is the addition of bromide to the developer, since the addition of bromide greatly retards development, and it is found that the higher

the reduction potential of a developer, the more bromide is required to produce a given effect. If we measure the developing agents in this way, we shall find that hydroquinone has the lowest reduction potential, then Athenon, then pyro, then Kodelon, and finally Elon, which has the highest. Hydroquinone has so low a potential that it is rarely used alone but is generally used with Elon. Kodelon can be substituted for Elon but more Kodelon has to be used in order to produce a developer of the same strength. Developers with a high reduction potential such as Elon, and to a less extent Kodelon, make the image flash up all over at once, because they start development very quickly even in the lesser exposed portions of the emulsion, while developers of low reduction potential, like pyro and especially hydroquinone, bring up the highlights of the image first and the shadows do not fully appear until the highlights are somewhat developed.

Most developing agents cannot develop at all when used by themselves. With the exception of Acrol, developing agents, in order to do their work, must be in an alkaline solution, and the energy depends upon the amount of alkali present. The developers of higher reduction potential, which bring up the image very quickly, require less alkali than those of lower reduction potential. For instance, hydroquinone is often used with caustic alkalis, while the other developing agents require only the weaker carbonated alkali.

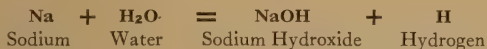
The quantity of alkali governs the energy of a developer, and if too much alkali is present, the developer will tend to produce chemical fog, while if too little alkali is present, it will be slow in its action. Alkalis also soften the gelatin of the emulsion, and consequently too alkaline a developer will produce over-swelling and will give trouble with frilling or blisters in warm weather.

The alkalis most commonly used in development are of two kinds: the caustic alkalis and the carbonated alkalis.

Caustic alkalis are produced when the metal itself reacts with water, the metals from which the alkalis generally used are derived being potassium and sodium. These metals are so easily oxidized that they have to be preserved from all contact with air or water by immersion in light oil or gasoline.

If we take a small piece of sodium and place it on the surface of water in a dish, it will react with the water with great violence, melting with the heat produced and sputtering about the surface; while if we restrict its movement, the

development of heat will be so great that the hydrogen produced will burst into flame. In the case of potassium, the reaction is even more violent than with sodium and is always accompanied by flame. The reaction may be represented by the equation—



the sodium combining with the water to form caustic soda and liberating hydrogen, which comes off as gas, and, as has already been stated, catches fire and burns in the air. This is, of course, not the method by which the alkalis are actually produced. As a matter of fact, the metals are produced by electroplating the metal out from the melted alkali.

SODIUM HYDROXIDE (CAUSTIC SODA) is made either by the passage of an electric current through a solution of common salt, when the soda separates at one electrode and chlorine gas is liberated at the other, or from sodium carbonate, which is causticized by means of lime. Lime is calcium oxide and is prepared by heating limestone, which is calcium carbonate, the carbon dioxide being driven off from the limestone by the heat. When the lime is added to sodium carbonate, the lime removes the carbon dioxide from the carbonate, and leaves the sodium hydrate in the solution, which is then evaporated to get the solid substance. At present, caustic soda is easily obtained in a very pure state, and there is usually no difficulty in getting good caustic soda for photographic work. It must be protected from the air, since it easily absorbs moisture and carbon dioxide. As its name indicates, it is very caustic and attacks the skin, clothing, etc.

POTASSIUM HYDROXIDE (CAUSTIC POTASH) is very similar to caustic soda and is prepared in the same way. Fifty-six parts of caustic potash are chemically equivalent to forty parts of caustic soda.

Both caustic soda and caustic potash should be dissolved in cold water when solutions of either chemical are prepared, because on mixing considerable heat is evolved and the solution, if too hot, is apt to boil and spatter on the hands or face causing serious burns.

An alkali which was often used with pyrogallol in the early days of photography, but which is rarely used nowadays, is ammonia. Nitrogen combines with three times its volume of hydrogen to form a gas, NH_3 . This gas is known as ammonia and is very soluble in water, its solution being strongly alkaline. Ammonia combines directly with acids to form salts which are analogous to the salts of sodium and potassium. Thus with hydrochloric acid it forms ammonium chloride, which is similar to sodium chloride and potassium chloride:



Ammonia is a somewhat weaker alkali than soda or potash but stronger than the carbonates. For use in development it has the disadvantage that being used in the form of a solution of a gas its strength is somewhat uncertain and variable, the ammonia escaping from the solution. Also, it is a solvent of silver bromide and tends to produce colored stains which are not so easily produced with other alkalis.

AMMONIA SOLUTION is commercially prepared from the ammoniacal liquor obtained in the distillation of coal for coal gas. The liquor is neutralized with sulphuric acid, the ammonium sulphate crystallized out, and the ammonia gas liberated from the sulphate with lime and led into water, in which it dissolves. The solution is usually free from impurities.

Ammonia solutions are prepared commercially in two strengths, "ammonia water," containing 10% of ammonia gas by weight and having a specific gravity of 0.96, and "stronger ammonia water" containing 28% of ammonia by weight and having a specific gravity of 0.90.

The alkalis generally used for photographic work are not the caustic alkalis but the carbonates, which are salts of carbonic acid, H_2CO_3 . Carbonic acid is a very weak acid, so that in solution the carbonates are not neutral but alkaline because of the predominance of the strong base over the weak acid, the carbonate being, to some extent, split up into the bicarbonate or acid carbonate and the caustic alkali. The use of a carbonate in development therefore represents a sort of reservoir of alkali, only a small quantity of alkali being present at any time, but more being generated by dissociation of the carbonate as it is used up. If instead of using carbonate we were to use for development a solution containing a proportional quantity of caustic alkali, we should have only a small quantity of alkali present, and it would soon be exhausted. The use of carbonate, therefore, enables us to employ a small concentration of alkali and yet to keep that concentration nearly constant during use.

When a salt is dissolved in water at a high temperature until no more will dissolve and then the solution is allowed to cool, the salt will generally be deposited in crystals; sometimes, as in the case of silver nitrate, the crystals consist of the pure substance, but more often each part of the salt combines with one or more parts of water to form the crystals. This combined water is called "water of crystallization." Thus, crystals of sodium carbonate formed from a cool solution contain ten parts of water to one of carbonate, and their composition should be written:



What is called in the last paragraph a "part" of sodium carbonate, Na_2CO_3 , will weigh 106 units, while a "part" of water, H_2O , weighs 18 units, so that the crystals of sodium carbonate contain 106 parts by weight of sodium carbonate and 180 by weight of water, and consequently crystallized sodium carbonate contains only 37% of dry sodium carbonate. If sodium carbonate is crystallized from a hot solution only one part of water is combined in the crystals with each part of sodium carbonate so that they have the composition $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ and contain 85% of dry carbonate. Sodium carbonate containing ten parts of water of crystallization loses nine of them by drying in the air and breaks up, forming the compound with one part of water. This last part of water is only removed with difficulty by heating in the air, when the dry carbonate is formed, containing only a small residual quantity of water and about 98% carbonate.

When exposed to the air chemicals often either absorb or give up water. Those which absorb water are said to be "hygroscopic," and if they absorb so much that they dissolve and form a solution they are said to be "deliquescent." Chemicals which give up water to the air, so that the crystals break down and become covered with powder, are called "efflorescent."

SODIUM CARBONATE comes on the market in three forms: Crystals with ten parts of water, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ containing 37% of the carbonate; crystals with one part of water, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, containing 85% of the carbonate, and the dry powder containing 98% of the carbonate. The carbonate is made by treatment of salt solution with ammonia and carbon dioxide which reacts with the salt to produce sodium bicarbonate, NaHCO_3 . The bicarbonate is heated and half of the carbonic acid driven off, producing crude sodium carbonate, which at this stage is known as "soda ash." This is then dissolved in water, and crystals of "sal soda," containing ten parts of water, are produced. From this a crystalline salt with either one or ten parts of water is prepared for photographic use, but owing to the uncertainty of the composition of these crystals it is better to prepare the pure dry carbonate. This is obtained by heating the pure bicarbonate which can be precipitated from a solution of sal soda by means of carbon dioxide gas. When the bicarbonate is heated in the air, half of the carbonic acid is driven off, and sodium carbonate, Na_2CO_3 , is produced according to the equation:



The exact amount of heating is very important. If it is not done for sufficient time there will be a large quantity of bicarbonate left in the product, and bicarbonate is practically useless as an alkali in photography. On the other hand, if heating is continued too long, caustic soda will be produced. In the preparation of photographic carbonate the heating should be continued so that the material is almost pure sodium carbonate containing prac-

tically no bicarbonate but is very slightly on the alkaline side. Much caustic soda would be fatal, but it is better to have a trace of caustic soda than bicarbonate. The preparation of sodium carbonate is a matter to which the greatest attention is given by the Eastman Kodak Company, and the E. K. Tested Carbonate is specially prepared to meet the needs of the photographer.

POTASSIUM CARBONATE is sometimes used instead of sodium carbonate in developer formulas. Although it is more soluble than sodium carbonate, it has the disadvantages of being more expensive and absorbs water very readily. It must, therefore, be kept in well-sealed bottles.

Another alkali which has come into extensive use recently is borax. This chemical is recommended for use in a developer especially suited for the production of fine grained motion picture negatives. Every photographic image is composed of tiny coke-like masses of silver which have been reduced from the original crystals of silver bromide in the sensitive emulsion. The advantage of keeping the particles as small as possible is obvious, especially in motion picture work where the individual pictures comprising a film are enlarged several hundred times during projection. One of the causes of "graininess" or the coarsening of these tiny particles in the picture image is the fusion or clumping of the grains which occurs during development. Experiments have shown that several silver halide crystals in close proximity to each other, even though unexposed, may become developed and form a clump as a result of actual contact with an exposed crystal.

In the special developer (Formula D-76, page 52) there is a high concentration of sulphite which is a solvent for silver bromide and iodide. As development progresses therefore, the sulphite actually dissolves a small quantity of each grain and thereby minimizes greatly the tendency for clump formation which would increase the graininess. Addition of carbonate to such a developer increases the rate of development and also accentuates the graininess of the resulting negative.

BORAX or SODIUM TETRABORATE is prepared from certain calcium ores by first roasting, then boiling in sodium carbonate and bicarbonate solution, and finally crystallizing in large iron vats. A new source of borax discovered in Kern County, California in 1926 is virtually pure sodium borate and requires only dissolving, filtering, and recrystallizing to prepare it for the market. The pure salt forms large crystals readily soluble in hot water. It is used in developers for the production of fine grained negatives and in acid hardeners for prints which are to be dried on belt driers.

Owing to the fact that developers are necessarily substances which have a great affinity for oxygen and that the

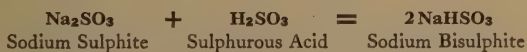
air contains oxygen, developing solutions containing only the developing agent and alkali would be rapidly spoiled from oxidation by the air. In order to make the developer keep there is added to the developing solution, in addition to the reducing agent and alkali, some sodium sulphite. Sodium sulphite has a very strong affinity for oxygen, being easily oxidized to sodium sulphate (see page 10), so that it protects the developer from the oxygen of the air, thus acting as a "preservative." This action of the sulphite is very easily seen with the pyrogallol developer. The oxidation product of pyrogallol is yellow, and this oxidation product which is formed in development is deposited in the film along with the silver, so that if we use a pyrogallol developer without sulphite we shall get a very yellow negative, the image consisting partly of silver and partly of the oxidized pyrogallol. If we use sulphite in the developer, the image will be much less yellow because the pyrogallol will be prevented from oxidizing, the sulphite being oxidized instead, and finally if we add a great deal of sulphite, we shall get almost as blue an image as with Elon, the oxidation product of which is not deposited in a colored form with the silver.

SODIUM SULPHITE is prepared by blowing sulphur dioxide gas into a solution of sodium carbonate. When sulphite is crystalized from the cooled solution it forms crystals containing seven parts of water to one of sulphite, of the composition $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ which contain, when pure, 50% of dry sulphite. These crystals give up water when kept in the air and form a white powder on the surface. Since sulphite, when exposed to the air, has a tendency to oxidize to the sulphate, and as the sulphate is not a preservative, it is well to view with suspicion sulphite which has effloresced to a great extent. A quick rinse in cold water will remove the white powder from the crystals.

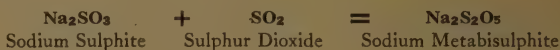
Sulphite free from water is produced by two methods: by drying the crystals, which produces what is called the "desiccated" salt, containing about 92% of pure sulphite, and by precipitation from hot solutions which gives a compound generally called "anhydrous" sulphite, and which contains as much as 96.5% of sulphite.

Eastman Tested Sulphite is the desiccated salt, and is prepared in a pure state almost free from sulphate. If prepared in this way as a dry powder the sulphite will keep well for a long time.

Sodium forms a number of compounds with sulphurous acid in addition to sodium sulphite itself. Thus there is sodium acid sulphite or bisulphite, NaHSO_3 , which may be regarded as a compound of sodium sulphite with sulphurous acid:



Another, sodium metabisulphite, is a compound of sodium sulphite with sulphur dioxide:



Ordinary commercial bisulphite has been shown by analysis to consist chiefly of metabisulphite which is converted into bisulphite when dissolved in water. Commercially dry sodium bisulphite is supplied by the Eastman Kodak Company in a very pure form as one of its Tested Chemicals. It may be used with entire confidence when mixing formulas calling for either metabisulphite or bisulphite.

POTASSIUM METABISULPHITE is often used as a preservative. It forms good crystals and is convenient to use but is very costly in comparison with sodium bisulphite.

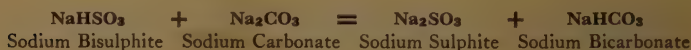
SODIUM BISULPHITE, when pure, is a white salt which has an acid reaction, often containing a slight excess of sulphur dioxide. Since sodium sulphite is an alkaline salt, owing to the predominance of the strong base, soda, over the weak sulphurous acid, a neutral solution can be produced by adding a small quantity of bisulphite to sulphite, and this neutral solution has found extensive application as a preservative for a pyro developer. Bisulphite is used very largely as a preservative for fixing baths, supplying both the sulphite and the acid necessary.

It is difficult to prepare bisulphite free from iron, and any iron in the bisulphite produces a dark color when used for making up a pyro solution.

It is often customary to substitute sodium bisulphite for potassium metabisulphite weight for weight. It really simmers down to a matter of dollars and cents because either chemical is quite satisfactory for the purpose but, as a rule, sodium bisulphite ranges in cost from *one-third* to *one-half* that of potassium metabisulphite.

Since sodium bisulphite may be considered as a compound of sodium sulphite and sulphurous acid, while sodium sulphite is alkaline, bisulphite is preferable as a preservative in the case of a two-solution developer, since oxidation progresses less readily in acid than in alkaline solution.

In the case of a one-solution developer containing, say, sodium sulphite, sodium bisulphite and sodium carbonate, the bisulphite is converted to sulphite by the sodium carbonate according to the following equation:



The sodium bisulphite neutralizes or destroys an equivalent quantity of sodium carbonate, thus reducing the proportion of alkali and therefore exerts an apparent restraining action, while the developer apparently keeps longer because some of the carbonate has been destroyed.

It might be thought from the above equation that it would be as effective and perhaps simpler to use only sodium sulphite instead of sulphite and bisulphite, but experiments have shown that the bicarbonate formed, acts as an anti-fogging agent.

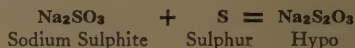
A further discussion of the properties of developers is given under Chapter X, page 83.

CHAPTER IV.

The Chemistry of Fixation

After development, the undeveloped silver bromide is removed by immersion of the negative or print in what is called the "fixing" bath. There are only a few substances which will dissolve silver bromide, and the one which is universally used in modern photography is sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$, which is known to photographers as hyposulphite of soda, or more usually as hypo, though the name hyposulphite of soda is used by chemists for another substance.

SODIUM THIOSULPHATE or **HYPO** can be made by boiling together sodium sulphite and sulphur, the sulphur combining with the sodium sulphite according to the equation.

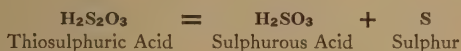


In practice it is generally made from calcium sulphite residues, the calcium thiosulphate being then converted into the sodium salt by treatment with sodium sulphate. The hypo comes on the market in clear crystals and is usually fairly pure, any foreign substance present being more often due to accidental contamination than to its chemical nature and consisting of dirt, straw or wood dust due to careless handling. Sometimes, however, the hypo contains calcium thiosulphate, which decomposes much more readily than the sodium salt. On the whole, it is not difficult to obtain good hypo; the Eastman Tested Hypo is prepared in the form of granular crystals, easy to dissolve, and free from accidental contamination.

Fixing is accomplished by means of hypo only, but materials are usually transferred from the developer to the fixing bath with very little rinsing so that a good deal of developer is carried over into the fixing bath, and this soon oxidizes in the bath, turning it brown, and staining negatives or prints. In order to avoid this the bath has sodium sulphite added to it as a preservative against oxidation, and the preservative action is, of course, greater if the bath is kept in a slightly acid state. In order to prevent the gelatin from swelling and softening it is also usual to add some hardening agent to the fixing bath so that a fixing bath instead of containing only hypo will contain in addition sulphite, acid, and hardener.

If a few drops of acid, such as sulphuric or hydrochloric acid are added to a weak solution of hypo, the hypo will be

decomposed and the solution will become milky, owing to the precipitation of sulphur. This is because the acid converts the sodium thiosulphate into the free thiosulphuric acid, and this substance is quite unstable, decomposing into sulphurous acid and sulphur according to the equation:



The change of thiosulphate into sulphite and sulphur is reversible, since, if we boil together sulphite and sulphur we shall get thiosulphate formed, so that while acids liberate sulphur from the hypo, sulphite combines with the sulphur to form hypo again. Consequently, we can prevent acid decomposing the hypo if we have enough sulphite present, since the sulphite works in the opposite direction to the acid. An acid fixing bath, therefore, is preserved from decomposition by the sulphite, which also serves to prevent the oxidation of developer carried over into it. The developer which is carried over into the fixing bath is, however, alkaline and consequently a considerable quantity of acid is required in a fixing bath which is used for any length of time, since if only a small quantity is present, it will soon be neutralized by the developer carried over. We are, therefore, in the difficult position that we require a large quantity of acid present, and yet the fixing bath must not be strongly acid. The solution of the difficulty is found by taking advantage of the fact that there are some acids which are very weak in their acidity and yet can neutralize alkali in the same way as a strong acid, so that a large quantity of these acids can be added without making the bath so acid that sulphur is precipitated.

The strength of an acid depends upon the fact that when it is dissolved in water some of the hydrogen contained in it dissociates from the acid and remains in the solution in an active form, and the acidity of the solution depends upon the proportion of the hydrogen which is dissociated into this active form. The quantity of alkali which the acid can neutralize, however, depends upon the total quantity of the hydrogen present, and not on the dissociated portions only. The strongest acids are the mineral acids, such as sulphuric and hydrochloric while the weakest acids are the organic acids, such as citric and acetic acids.

Since a large quantity of a weak acid is required, the best acid for the purpose is acetic acid.

ACETIC ACID is prepared by the fermentation of apple juice, yielding a product commonly called vinegar. In addition to acetic acid, vinegar also contains many impurities and the acid strength is from 4% to 8%. The stronger acid is made from acetate of lime which is prepared either by neutralizing vinegar with chalk or, more commonly, by neutralizing with lime the crude acetic acid prepared by the destructive distillation of wood. Acid thus prepared may contain as high as 99.5% acetic acid and is usually called glacial acetic acid because, at moderately low temperatures, it freezes to a solid. Dilutions of the glacial acid are commonly supplied containing 80% and 28% acetic acid. This 28% acetic acid, prepared by diluting three parts of pure glacial acetic acid with eight parts of water, must not be confused with "commercial 28% acetic acid" which is prepared by redistilling the acid obtained by the destructive distillation of wood.

When acetic acid cannot be obtained for the fixing bath, the only substitute which appears to be generally available is sodium bisulphite, NaHSO_3 . This compound is intermediate between sodium sulphite and sulphurous acid, and is, therefore, equal in acidity to a mixture of equal proportions of these two substances. It makes a satisfactory acid fixing bath but does not give quite as good a reserve of available acid in the bath as acetic acid does. This is of importance particularly in connection with the hardening agent used in the fixing bath.

The commonest hardening agent is potassium alum, the alums having the property of tanning gelatin.

ALUMS are compound sulphates consisting of sodium, potassium or ammonium sulphate with aluminum sulphate. They have the general formula $\text{R}_2\text{SO}_4, \text{M}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, where R may be an alkali metal or the ammonium radical, and M is chromium or aluminum. If the hydrogen in sulphuric acid be replaced by potassium, we get potassium sulphate, K_2SO_4 , while if it be replaced by aluminum, we get aluminum sulphate, $\text{Al}_2(\text{SO}_4)_3$. The aluminum sulphate combines with other sulphates to form the alums, of which the commonest are potassium alum and ammonium alum. Sodium alum does not crystallize well, but the potassium and ammonium salts crystallize in large, clear crystals. They are almost always sold in the form of very fine crystals, to facilitate weighing and to prevent lumping which occurs with powdered alums.

POTASSIUM CHROME ALUM, $\text{K}_2\text{SO}_4, \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, which is often used in the place of ordinary alum, does not contain any aluminum in spite of its name. It is a compound sulphate of potassium sulphate with chromium sulphate, of which the formula is $\text{Cr}_2(\text{SO}_4)_3$, the chromium taking the place of the aluminum present in aluminum sulphate. Chrome alum is prepared commercially in large quantities and of a high degree of purity. It occurs as violet crystals soluble in water, its solution in cold water being violet but going green on heating owing to the change in the composition of the salt.

AMMONIUM CHROME ALUM $(\text{NH}_4)_2\text{SO}_4, \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, is chemically very similar to potassium chrome alum except that it is the compound of ammonium sulphate with chromium sulphate. Despite its very

close chemical similarity to the potassium compound if a fixing bath containing ammonium chrome alum becomes alkaline ammonia gas is evolved which produces a greenish sheen on the surface of the emulsion known as "dichroic" fog. This warning is given because at times, due to price fluctuations, the use of ammonium alum is sometimes slightly advantageous from the point of view of dollars and cents, but it is always safer to use a potassium salt even though it may cost one or two cents a pound more.

In the presence of sodium sulphite a solution of chrome alum loses its hardening properties somewhat rapidly, depending upon the concentration of the chrome alum and the sodium sulphite. A fresh chrome alum fixing bath containing hypo, chrome alum, sulphite and sulphuric acid loses its hardening properties in the course of one or two days even if the bath is not used. A chrome alum fixing bath containing from 1 to 2% chrome alum is only useful when used immediately after preparation, although a bath containing from 5% to 10% chrome alum will maintain its hardening properties for two or three days. Chrome alum is most useful as a hardening bath between developing and fixing. A plain solution of chrome alum retains its hardening properties indefinitely, though with use when developer is carried over by the plates and films, the hardening properties of the bath fall off owing to the presence of sodium sulphite in the developer.

Formalin is sometimes suggested as a hardening agent in fixing baths for hot weather processing. It should be used only in alkaline or neutral solutions because in acid solutions, it does not harden. With certain individuals, formalin irritates the mucous membranes of the nose and throat and its use, therefore, is very objectionable.

FORMALIN is a solution of formaldehyde, a gas having a very strong odor. The commercial solution contains 40% of formaldehyde and has the property of hardening gelatin very powerfully, a 5% solution rendering the gelatin of a film completely insoluble in boiling water in less than a minute.

The characteristics of fixing baths are discussed further under Chapter X, page 89.

CHAPTER V.

The Chemistry of Washing

It may seem strange that a chapter dealing with washing should be inserted in a book on photographic chemistry, because washing is not usually regarded as a chemical operation. Nevertheless, the laws governing washing are distinctly chemical in their nature, and the importance of washing in photography justifies greater attention than is usually paid to the subject.

As a general rule the object in washing negatives or prints is to remove from them the chemicals of the fixing bath which they contain. In the first place, it must be pointed out that it should not be necessary to wash out silver compounds but only the chemicals of the fixing bath. If an exhausted fixing bath is used silver compounds will be present during washing and must be removed very completely, so that if work has to be hurried and the time of washing must be cut down, it is most important that fixing should be complete.

The best way of insuring complete fixing is to use two fixing baths, and to transfer the negatives or prints to the second bath after they have been fixed in the first. Then, when the first bath begins to show signs of exhaustion and refuses to fix quickly, it should be replaced by the second, and the new, clean fixing bath should be used in the place of the second bath again.

The rate of washing depends largely upon the rate of diffusion of the hypo out of the film into the water providing the water in contact with the film is continuously removed. This diffusion rate has nothing to do with solubility. The solubility of a substance fixes the proportion of the substance which can go into solution.

There are a number of errors which are current concerning washing. It is commonly believed, for instance, that plates and paper can be washed more rapidly in warm water than in cold. This is a mistake. It is true that any salt will diffuse more rapidly in warm water than in cold, but when washing a photographic material the diffusion has to take place in gelatin, and the warmer the water in which the gelatin is placed, the more it swells, and its swelling hinders diffusion

in about the same proportion as the rise in temperature accelerates it, so that, as a matter of fact, washing goes on at about the same rate at all ordinary temperatures.

It is sometimes stated that material which has been hardened in the fixing bath washes more slowly than material which has not been hardened. This, too, is incorrect. Gelatin is like a sponge; the effect of hardening it is to contract all the network of the sponge, but in so doing the gelatin as a whole is not contracted and there is no difference in the diffusion between gelatin, which has not been hardened and which has been hardened, unless the gelatin has been dried after hardening. If a negative is thoroughly hardened in the fixing bath and then is dried down, it will not expand much when soaked again and consequently diffusion through it will be difficult, but before drying the hardening does not affect diffusion and the materials which wash most quickly are those in which the gelatin has not been swollen in its treatment, either in development or fixation, but has been kept in a firm, solid condition.

The actual rate of washing may be understood by remembering that the quantity of hypo remaining in the gelatin is continually halved in the same period of time as the washing proceeds. An average negative, for instance, will give up half its hypo in fifteen seconds when washed directly under the faucet, so that at the end of fifteen seconds half the hypo will be remaining in it, after thirty seconds one-quarter, after forty-five seconds one-eighth, after one minute one-sixteenth, and so on. It will be seen that in a short time the quantity of hypo remaining will be infinitesimal. This, however, assumes that the negative is continually exposed to fresh water, which is the most important matter in arranging the washing of either negatives or prints.

In most trays and washing tanks an average negative will give up half its hypo in 30 seconds. The process will then stop unless the water in the vessel is changed. The rate of washing thus turns out to be dependent firstly, on the degree of agitation, and secondly, on the rate of removal of the used water. This rate is dependent directly on the ratio of the stream of water falling into the vessel and the size of the vessel, quickest renewal taking place when the vessel is small and the stream large.

Only exact experimental measurements will tell when a particular vessel and stream of water will wash a specific kind of film or paper.

However, as a rough and safe working guide, the washing power of the vessel may be judged by noting the time it takes colored water to be replaced by colorless water from the faucet. To this time the minimum washing time for the material is added, and the total taken to indicate the actual period to be allowed by the photographer under his particular conditions.

A practical example will make the matter clear. Suppose that a large tray is resting in the sink and water is falling into it from the faucet and flowing to waste over the sides. Into the tray, and while the water is running, an ounce of 1% potassium permanganate solution or red ink is poured in and the time noted for the water to become completely colorless. To this time is added the minimum washing time of the material, a representative list of which is given below:

Lantern slide plates	3 minutes
Other plates	5 minutes
Film negatives, all kinds	about 7 minutes
Single weight Velox	15 to 20 minutes
Single weight Bromide	20 to 25 minutes
Double weight Bromide	35 to 60 minutes

If it be found that the water in the tray takes 10 minutes to clear, then the time for a lantern plate to become thoroughly washed would be 13 minutes and for Velox about 25 minutes. If the water supply were doubled and the rate of color discharge shortened to 5 minutes the washing times would be 8 minutes and 20 minutes respectively. Finally, if the lantern plate were held under an open faucet in the hand, the renewal of water at the emulsion surface would be extremely rapid and the plate would be *safely washed in 3 minutes*. The moral is to use plenty of water and plenty of agitation.

If a lot of prints are put in a tray and water allowed to splash on the top of the prints, it is very easy for the water on the top to run off again, and for the prints at the bottom to lie soaking in a pool of fairly strong hypo solution, which is much heavier than water and which will fall to the bottom of the tray. If the quickest washing is desired, washing tanks should be arranged so that the water is changed continuously and completely and the prints or negatives are subjected to a continuous current of fresh water. If water is of value, and it is desired to economize in its use, then by far the most effective way of washing is to use successive

changes of small volumes of water, putting the prints first in one tray for two to five minutes, and then transferring them to an entirely fresh lot of water, and repeating this procedure about six times.

Now a word of warning about contaminating partly washed photographs. If the hypo comes out to half its previous strength in a fraction of a minute, so also will the reverse change occur. If a partly washed print is touched by fingers contaminated with the fixing bath, in a few seconds the hypo will be shared between the fingers and the photograph, and it will take the full washing time to remove it again.

Since hypo is invisible and its evil effects are not detected till long afterwards, prints or films fresh from the hypo should never be placed among those partly washed. If this is done the entire batch must be washed from the time that the last one was added.

The best way to avoid contamination is to wash in *cascade*. In its simplest form this can be accomplished by placing two trays side by side, one an inch or so above the level of the other. Water is allowed to run into the upper tray and overflow into the lower. All prints and films should be placed in the lower tray before transference to the upper. The operator should also use the lower tray for washing hypo off his fingers. The prints and films should have at least three minutes preliminary washing before going into the true washing tray. With a little experience in handling materials in this serial order the photographer will be surprised at the number of films and papers that can be passed through quite moderate capacity trays and completely satisfactory washing secured in a short time.

The progress of washing can be followed by removing two or three prints at intervals from the bath and testing for hypo by using the hypo test formula, directions for which are given on page 57. An even simpler test is to taste the prints since hypo containing silver has a sweet taste.

Six changes of water, allowing five minutes for each change, should be sufficient to eliminate the hypo effectively from any ordinary photographic material.

CHAPTER VI.

The Chemistry of Reduction and Intensification

Reduction

By *reduction* in photography is meant the removal of some silver from the image so as to produce a less intense image. Thus, in the case of an over-developed film or plate there will be too much density and contrast, and the negative may be reduced to lessen this. In the case of an over-exposed negative there may not be an excess of contrast but the negative will be too dense all over, and in this case what is required is the removal of the excess density.

It is unfortunate that the word "reduction" is used in English for this process. In other languages the word "weakening" is used, and this is undoubtedly a better word, because the chemical action involved in the removal of silver from a negative is oxidation, and the use of the word reduction leads to confusion with true chemical reduction, such as occurs in development.

All the photographic reducers are oxidizing agents, and almost any strong oxidizing agent will act as a photographic reducer and will remove silver, but various oxidizing agents behave differently in respect to the highlights and shadows of the image. Reducing solutions can be classified in three classes:

- A. Cutting reducers
- B. True scale reducers
- C. Flattening reducers.

A. THE CUTTING REDUCERS remove an equal quantity of silver from all parts of the image, and consequently remove a larger proportion of the image from the shadows than from the highlights of the negative. The typical cutting reducer is that known as *Farmer's Reducer*, consisting of a mixture of potassium ferricyanide and hypo, the potassium ferricyanide oxidizing the silver to silver ferrocyanide and the hypo dissolving the latter compound. Farmer's Reducer will not keep when mixed, decomposing rapidly, so that it is usually

prepared by making a strong solution of the ferricyanide and then adding a few drops of this to a hypo solution when the reducer is required. It is especially useful for clearing negatives or lantern slides which show slight fog, and is also used for local reduction, the solution being applied with a brush or a wad of absorbent cotton. (See formula R-4, p. 58.)

Another cutting reducer is permanganate. The permanganates are very strong oxidizing agents, and if a solution of permanganate containing sulphuric acid is applied to a negative, it will oxidize the silver to silver sulphate, which is sufficiently soluble in water to be dissolved. (See formula R-2, p. 58.)

Permanganate has only a very weak action on a negative if no acid is present and this may be made use of for the removal of "dichroic" fog, the yellow or pink stain sometimes produced in development. Dichroic fog consists of very finely divided silver and this is attacked by a solution of plain permanganate (about 0.25%) which will have no appreciable action on the silver of the image.

An important difference should be noted between the behavior of ferricyanide and permanganate when used for reducing pyro-developed negatives. In a negative developed with pyro the image consists partly of the oxidation product of the pyro associated with the silver. (See p. 25). When such a negative is reduced with ferricyanide the silver is removed but the stain is unattacked so that the negative appears to become yellower during reduction, though the ferricyanide does not really produce the color, only making it evident by removal of the silver. Permanganate, on the other hand, attacks the stain image in preference to the silver and consequently makes the negative less yellow. Permanganate can also be used as an alternative to ferricyanide for bleaching negatives, since if bromide be added to the solution, silver bromide will be formed and the same bleaching action obtained as with ferricyanide.

POTASSIUM PERMANGANATE occurs in dark purple crystals which dissolve to form a purple solution. It is easily obtained pure but there is a good deal of impure permanganate on the market; Eastman Tested Permanganate is a pure product.

In addition to its use for reduction and bleaching, permanganate is employed as a test for hypo, since it is at once reduced by hypo, and the colored solution of the permanganate, therefore, loses its color in the presence of any hypo.

It may consequently be used to test the thoroughness of the elimination of hypo from negatives or prints in washing. When permanganate is reduced in the absence of an excess of free acid, a brownish precipitate of manganese dioxide is obtained and sometimes negatives or prints which have been treated with permanganate are stained brown by this material. Fortunately, manganese dioxide is removed by bisulphite, which reduces it still further, forming a soluble manganese salt. The brown stain can, therefore, be removed by immersion of the stained material in a solution of bisulphite.

A very powerful cutting reducer is made from a solution of iodine in potassium iodide, to which potassium cyanide has been added to dissolve the silver iodide formed during reduction. Iodine is not soluble in water but is soluble in a solution of potassium iodide. To make up the reducer a few iodine crystals are dissolved in a 10% solution of potassium iodide, and five parts of this are added to one part of a 10% solution of potassium cyanide, making up to 100 parts with water for use.

B. **PROPORTIONAL REDUCERS** are those which act on all parts of the negative in proportion to the quantity of silver present there; hence they exactly undo the action of development, since during development the density of all parts of the negative increases proportionally. A correctly exposed but over-developed negative should be reduced with a proportional reducer. Unfortunately, there are no single substances which form exactly proportional reducers, but by mixing permanganate, which is a slightly cutting reducer, with persulphate, which is a flattening reducer, a proportional reducer may be obtained. (See formula R-5, p. 58.)

C. **FLATTENING REDUCERS** are those which act very much more on the heavy deposits than on the light deposits of the negative, and which will consequently reduce the highlights without affecting the detail in the shadows. Only one such reducer is known, and this is ammonium persulphate. Ammonium persulphate is a powerful oxidizing agent and attacks the silver of the negative, transforming it into silver sulphate, which dissolves in the solution. It must be used in an acid solution and is somewhat uncertain in its behavior, occasionally refusing to act, and always acting more rapidly as the reduction progresses. (See formula R-1, p. 57.)

AMMONIUM PERSULPHATE is a white crystalline salt, stable when dry. It has been found in the Research Laboratories of the Eastman Kodak

Company that the action of persulphate depends largely upon its containing a very small quantity of iron salt as an impurity, and that its capricious behavior is due to variations in the quantity of iron present. The persulphate supplied as an Eastman Tested Chemical may be relied upon to give a uniform action in reduction.

Intensification

Intensification is photographically the opposite of reduction, the object being to increase contrast. This is done by the deposition of some material on the silver image. A silver image, for instance, can be very much intensified by toning it with uranium (see page 44), the reddish-brown uranium ferrocyanide having very great printing strength and converting a weak negative into one having a great effective contrast for printing purposes. Usually, however, intensification is performed by depositing a silver, mercury or a chromium compound upon the image, and many photographic intensifiers depend upon the use of mercury. But experience has shown that mercury intensified images are not as stable as images produced by chromium intensification.

Mercury is a metal which forms two series of salts, the mercuric salts, which are in a higher degree of oxidation, and the mercurous salts.

Many of the mercuric salts are insoluble in water, but mercuric chloride is sufficiently soluble for practical use, and when a silver image is placed in a solution of mercuric chloride, this reacts with the silver and forms a mixture of mercurous chloride and silver chloride.

The bleached image, which appears white, can then be treated in various ways. If it is developed, for instance, both the silver chloride and the mercurous chloride will be reduced to the metal, and in addition to the silver, with which we started, we shall have added to every part of silver an equal part of mercury. Instead of using a developer we may blacken the image with ammonia, which forms a black mercury ammonium chloride and produces a high degree of intensification.

MERCURY BICHLORIDE or Mercuric Chloride is a virulently poisonous salt, sometimes known popularly as "corrosive sublimate." Its only use in photography is for intensification, and it is obtained in white, heavy crystals which are soluble with some difficulty in water. This may be obtained in satisfactory purity by ordering Eastman Tested Mercury Bichloride.

For many purposes separate bleaching and redevelopment is inconvenient, and for this reason the *Eastman Intensifier*

has been placed on the market, with which the intensification proceeds continuously so that it can be stopped at any time. This does not give quite so great an intensification as the use of the two solutions, but it is far more convenient in operation.

A very powerful method of intensification, used chiefly for negatives made by photo-engravers, is obtained by bleaching with mercuric chloride and blackening with silver dissolved in potassium cyanide. The use of the cyanide cuts the shadows very slightly at the same time that the highlights are intensified, so that a great increase in the contrast of the negative is obtained. This is usually known as the "*Monckhoven*" *Intensifier*.

In the case of the chromium intensifier the silver image is bleached with a solution of bichromate containing a very little hydrochloric acid, bichromate being an oxidizer of the same type as permanganate or ferricyanide. The image is then redeveloped and will be found to be intensified to an appreciable extent. This intensifier has found increasing favor owing to the ease and certainty of its operation and the permanency of the intensified image.

POTASSIUM BICHROMATE is made by the oxidation of chromium salts. It forms orange-red crystals, stable in air, and easily dissolves, yielding a yellow solution. It is obtained in a pure form by crystallization. Potassium bichromate is used in photography both for bleaching negatives and for sensitizing gelatin, fish glue, etc. When gelatin containing bichromate is exposed to light it becomes insoluble in water and in this way images may be obtained in insoluble gelatin.

CHAPTER VII.

The Chemistry of Toning

The operation of toning consists in the deposition on the silver image of another substance having a different color, in order to get a more pleasing result, or of the transformation of the silver image into another substance for the same purpose.

There are four principal methods of toning:

- A.* Toning by the replacement of the silver by other metals;
- B.* Toning by the deposition of salts of metals;
- C.* Toning by the transformation of the silver image into some substance to which dyes will attach themselves in an insoluble form;
- D.* Transformation of the silver image into a stable, strongly colored salt of silver.

A. In the case of prints which are made by the printing-out processes, the silver compound produced by the action of light is colored, and after fixation the image left is usually of an unpleasant color, a yellow or yellow-brown. In order to change this to a more satisfactory color it is toned by means of gold or, more rarely, platinum.

When a finely divided silver image is placed in a solution of gold or platinum the silver will replace the metal in solution, going into solution itself, and the gold or platinum will be deposited in the place of the silver. The rate at which these metals are deposited is very important, especially in the case of gold toning. If the gold is deposited too slowly, it will be deposited in a very fine condition, and in the case of finely divided metals, their color depends upon the fineness of the division. Finely divided gold is red, which is not as pleasing as the blue gold obtained by more rapid deposition.

To insure rapid deposition it is necessary that the bath should be kept alkaline, and consequently borax or sodium acetate is added to the gold chloride to make a toning bath, while sometimes substances having a weak reducing action are added, such as sulphocyanides or formates. Platinum toning baths are used in an acid condition.

The chemicals used for making up these toning baths must be of high purity, and it is best to get tested chemicals in all cases.

GOLD CHLORIDE is made by dissolving gold in a mixture of hydrochloric and nitric acids and evaporating the solution. It forms brownish crystals, rapidly absorbing water, which contains 65% metallic gold. The salt is sold in small glass tubes containing 15 grains, and in order to use it, the label is removed from the tube and the tube is broken in a bottle containing a known volume of water so that a solution of definite strength is obtained without danger of losing the precious material.

GOLD SODIUM CHLORIDE is a double chloride of gold and sodium which occurs in yellow crystals and contains 49% of metallic gold. It has the advantage over the pure chloride of gold that it is neither acid nor deliquescent.

POTASSIUM CHLOROPLATINITE is the double chloride of platinum and potassium, and is the form in which platinum is used for a toning bath. It occurs in reddish crystals, and is supplied in sealed glass tubes like gold chloride.

LEAD NITRATE and LEAD ACETATE. These colorless salts of lead are sometimes used for toning baths. They are both soluble in water and the solutions are very poisonous.

SODIUM ACETATE, SODIUM PHOSPHATE (Di-basic) and BORAX are all weak alkalis and are used in gold toning baths for this reason. They occur as white salts, soluble in water. Borax occurs as a mineral and is largely used in industry. Only the pure salt should be used for photographic purposes.

AMMONIUM SULPHOCYANATE, SULPHOCYANIDE OR THIO-CYANATE, is a salt occurring in very deliquescent crystals. In order to be at all certain of its strength it must be preserved with great care, out of contact with the air. It is one of the most popular salts for use with gold chloride in toning baths.

B. A good many metallic compounds are colored, and if the silver image is replaced by these colored compounds, wholly or in part, a colored image is obtained. In most of the toning processes based upon the use of colored compounds, ferrocyanides of metals are employed, the silver image being first transformed into silver ferrocyanide, the silver in the silver ferrocyanide being then substituted by another metal of which the ferrocyanide is colored.

The ferro- and ferricyanides are very complex compounds. The cyanides themselves are compounds containing carbon and nitrogen, and have a curious resemblance to chlorides and bromides. Hydrogen unites with carbon and nitrogen to form an acid, HCN, which is called *hydrocyanic acid*, or sometimes prussic acid. The hydrogen in this can be substituted by metals to form cyanides such as potassium cyanide, KCN,

which is analogous to potassium chloride, KCl , or potassium bromide, KBr , and on adding a solution of silver nitrate to a soluble cyanide, silver cyanide, $AgCN$, is precipitated as an insoluble salt, just as silver chloride or silver bromide is precipitated.

There is one respect, however, in which hydrocyanic acid and the cyanides differ from the corresponding chlorine or bromine compounds, and this is that they are extremely poisonous. *A few grains of cyanide swallowed will cause death.*

Cyanide solutions are solvents for the silver halides, forming soluble double compounds with the insoluble silver salts. Potassium cyanide is employed for fixing wet collodion plates, which, being made from silver iodide, are not easily fixed in hypo. Whenever cyanides are used by photographers, their extremely poisonous nature should be remembered and every possible precaution taken in keeping and using them.

The cyanides easily form complicated double compounds. With sulphur, for instance, they form sulphocyanides, and ammonium sulphocyanide has already been referred to as being used in gold toning baths. The cyanides unite with iron cyanides to form two important groups of compounds called *ferrocyanides* and *ferricyanides*. These differ from each other in their degree of oxidation, the ferricyanides being more highly oxidized than the ferrocyanides, so that when a ferricyanide is reduced a ferrocyanide is formed.

POTASSIUM FERROCYANIDE is yellow. It is infrequently known as "yellow prussiate of potash" and has very little application in photography.

POTASSIUM FERRICYANIDE or red prussiate of potash is prepared by passing chlorine gas into a solution of the ferrocyanide and is deposited from concentrated solution as red crystals. The crystals are soluble in water and give a yellow solution.

The value of ferricyanide in photography lies in the fact that ferricyanide oxidizes the silver image and forms silver ferrocyanide from it, so that if a negative is placed in a solution of ferricyanide, it is slowly bleached to silver ferrocyanide.

This property can be made use of in various ways. The silver ferrocyanide is soluble in hypo so that if we use a solution of potassium ferricyanide and hypo instead of plain potassium ferricyanide, we shall not get a white image but the silver image will be dissolved slowly, since it will be

converted into the silver ferrocyanide by the ferricyanide and then the silver compound formed will be dissolved in the hypo. This mixture of ferricyanide and hypo is known as *Farmer's Reducer*, and will be referred to in the next chapter. Again, if we add bromide to our ferricyanide solution, silver bromide is more insoluble than silver ferrocyanide and consequently the silver ferrocyanide as it is produced will be transformed into silver bromide. This operation of transforming a silver image into a bromide image is generally known as *bleaching*. If we combine with the potassium ferricyanide a salt of a metal which gives an insoluble colored ferrocyanide, then we shall get the silver ferrocyanide formed, and this will be converted into the ferrocyanide of the metal whose salt has been added to the bath. If we add an iron salt, such for instance as iron citrate, to the potassium ferricyanide, we shall get a blue iron ferrocyanide formed and the image will be toned blue. If we use uranium nitrate, we shall get the reddish-brown uranium ferrocyanide, while if we use copper citrate, we shall get the red copper ferrocyanide. Sometimes instead of using the metal salt in the same bath as the ferricyanide the operation is done in two steps, the silver being first bleached to silver ferrocyanide, which then combines with a salt of the metal to form the colored metallic ferrocyanide.

C. The range of colors which can be obtained by the use of colored metals or metallic compounds is rather limited, and in order to get a wider range, especially for motion picture and lantern slide work, experimenters have tried to find methods of using dyes and attaching them to the image.

It has been found that this can be done by transforming the silver image into silver iodide, which can be accomplished, for instance, by treatment of the image with a mixture of potassium ferricyanide and potassium iodide. The silver iodide image formed in this way will mordant basic dyes and attach them to the image so that the image assumes the color of the dye. The Kodak Research Laboratories have worked out a process in which instead of transforming the silver image into silver iodide, it is treated with a uranium mordanting bath and transformed into a mixture of uranium and silver ferrocyanides, and then the basic dyes are mordanted onto this image. Full particulars of this process are given in our booklet "Lantern Slides, How to Make and Color Them," supplied on request to the Service Dept., Eastman Kodak Company, Rochester, N. Y.

D. Silver sulphide is a very insoluble compound of silver, and consequently if a silver image or a silver halide salt is treated with sulphur or a sulphide respectively they will at once be transformed into silver sulphide. Silver sulphide has a color varying from light brown to black, according to its state of subdivision, and the transformation of the image into silver sulphide is by far the most popular method of toning developing-out paper prints, the prints so toned being generally known as "sepia" prints.

When great permanency is required prints should preferably be toned to a silver sulphide image since experience has shown that this form of silver is one of the most stable. There are two general methods of transforming the image into silver sulphide:

1. Direct toning, with the hypo alum bath; and
2. Bleaching and redevelopment.

1. As was explained in the chapter dealing with fixing, when an acid is added to a solution of hypo, it tends to precipitate sulphur. Now, a solution of alum in water is weakly acid, so that if alum is added to plain hypo without any sulphite present, the solution will, after a time, become turbid and precipitate sulphur. This solution of alum and hypo at the point where it is ready to precipitate the sulphur may be considered as having free sulphur in solution, and if prints are immersed in a hot solution of alum and hypo (about 120° F.) (49° C.), the silver image will be converted directly into silver sulphide and the prints will be toned brown. Two precautions are necessary in order to obtain successful results with the hypo-alum toning bath. The bath works best at a temperature of 120°-125° F. (49°-52° C.); if the temperature is allowed to rise much above 130° F. (54° C.) there is danger of blistering and bleaching of the image. A fresh bath tends to weaken the print, eating out the highlights. To prevent this a little silver must be added to the bath preferably in the form of silver chloride as given under the hypo-alum toning bath formula T-1a, page 60. A bath lasts for a long time, and as a general rule a hypo-alum bath which has been somewhat used works better than a fresh bath. The color of the final tone is related directly to the color of the original black and white image. Blue-black images give cold chocolate tones; olive green images give warm sepia tones.

2. It is rather troublesome to use a bath which has to be heated, so that while hypo-alum toning is used on the large

scale, smaller quantities of prints are commonly toned by bleaching the silver print in a bath of ferricyanide and bromide, and then treating the bleached print after washing, with sodium sulphide, which converts the silver bromide directly into silver sulphide. This process is quite satisfactory for use with amateur prints and enlargements.

SODIUM SULPHIDE occurs in white, transparent crystals, which have a strong affinity for water and quickly deliquesce unless kept carefully protected from the air. It is best kept in a strong stock solution. So much trouble has been caused by impure sodium sulphide that of recent years the Eastman Kodak Company has been supplying a sulphide which they have fused so that it will contain no moisture and be of definite purity. One part, by weight, of the fused sulphide is equivalent to three parts, by weight, (approx.) of the crystals. Fused sodium sulphide is a greyish white product but this color is not a sign of harmful impurities.

Sodium sulphide often contains impurities, chiefly iron, though by dissolving in hot water the iron sulphide separates out as a black sludge, leaving a clear solution which should be decanted. Old sodium sulphide often contains hypo, and if it is present in any considerable quantity, some of the silver bromide will be dissolved by the hypo and the print will lose strength in the highlights and give an inferior result.

All sulphides give off a certain quantity of hydrogen sulphide, which smells offensively, and which is extremely dangerous to unexposed photographic materials, since a very small quantity of hydrogen sulphide will convert enough of the silver bromide or chloride of the material into sulphide to produce a severe fog. No photographic materials should therefore be stored in a room where sulphides are kept or where sulphide toning is done.

It has already been explained that the color of silver sulphide depends upon its state of division, and since the state of division of the toned image depends upon that of the untoned image and this again upon the treatment of the material, it is evident that the exposure and development of the print will have an effect upon the result obtained. As a general rule, it may be stated that to get good colors in sulphide toning it is necessary that a print should have been fully developed but not over-exposed. If a trace of iron is present in the ferricyanide-bromide solution used as the bleach in the redevelopment process, for example, from a defective enameled tray, blue spots composed of ferric ferrocyanide are liable to form. This tendency to form spots is reduced to a minimum by adding potassium oxalate to the bleach bath since the blue iron salt is soluble in the oxalate. Acetic acid is added also, to prevent possible formation of blisters (see formula T-7a, page 60.

CHAPTER VIII.

Formulas

It is always best to use the formulas for solutions recommended in the instructions issued by the maker for the use of photographic materials; such formulas are often adjusted to the properties of the particular materials concerned and will give better and more certain results than can be obtained with any others. It is often convenient, however, to have available standard formulas, and the following are therefore given:

Developing Formulas for Films and Plates

Standard A. B. C. Pyro

[Formula
D-1]

Stock Solution A

	Avoirdupois	Metric
Sodium Bisulphite (E.K.Co.) . . .	140 grains	9.8 grams
Pyro	2 ounces	60.0 grams
Potassium Bromide	16 grains	1.1 grams
Water to make	32 ounces	1.0 liter

Stock Solution B

Water	32 ounces	1.0 liter
Sodium Sulphite (E. K. Co.)	3½ ounces	105.0 grams

Stock Solution C

Water	32 ounces	1.0 liter
Sodium Carbonate (E. K. Co.)	2½ ounces	75.0 grams

Dissolve chemicals in order given.

For Tray Development—

Take 1 part of A, 1 part of B, 1 part of C, and 7 parts of water. Develop about 7 to 9 minutes at 65° F. (18° C.).

For Tank Development—

Take 1 part of A, 1 part of B, 1 part of C, and 11 parts of water. Develop about 13 to 15 minutes at 65° F. (18° C.).

Two Solution Pyro Tray Developer

[Formula
D-21]

Stock Solution A

	Avoirdupois	Metric
Sodium Bisulphite (E. K. Co.) . . .	140 grains	9.8 grams
Pyro	2 ounces	60.0 grams
Potassium Bromide	16 grains	1.1 grams
Water to make	32 ounces	1.0 liter

Stock Solution B

Water	32 ounces	1.0 liter
Sodium Sulphite (E. K. Co.)	3½ ounces	105.0 grams
Sodium Carbonate (E. K. Co.)	2½ ounces	75.0 grams

For use, take 1 part of A, 1 part of B, and 8 parts of water. Develop about 6 minutes at 65° F. (18° C.).

Tank or Tray Developer (Elon-Pyro)

[Formula
D-7]

Stock Solution A

	Avoirdupois	Metric
Water (about 125° F.) (52° C.) . . .	16 ounces	500.0 cc.
Elon	¼ ounce	7.5 grams
Sodium Bisulphite (E. K. Co.) . . .	¼ ounce	7.5 grams
Pyro	1 ounce	30.0 grams
Potassium Bromide	60 grains	4.2 grams
Water to make	32 ounces	1.0 liter

Stock Solution B

Water	32 ounces	1.0 liter
Sodium Sulphite (E. K. Co.)	5 ounces	150.0 grams

Stock Solution C

Water	32 ounces	1.0 liter
Sodium Carbonate (E. K. Co.) . . .	2½ ounces	75.0 grams

For Tray Development—

Take 1 part of A, 1 part of B, 1 part of C and 8 parts of water. Develop about 5 to 7 minutes at 65° F. (18° C.).

For Tank Development—

Take 1 part of A, 1 part of B, 1 part of C and 16 parts of water. Develop about 9 to 12 minutes at 65° F. (18° C.).

Tank or Tray Developer (Elon-Hydroquinone)

[Formula
D-61a]

Stock Solution

	Avoirdupois	Metric
Water (about 125° F.) (52° C.) . . .	16 ounces	500.0 cc.
Elon	45 grains	3.1 grams
Sodium Sulphite (E. K. Co.)	3 ounces	90.0 grams
Sodium Bisulphite (E. K. Co.) . . .	30 grains	2.1 grams
Hydroquinone	85 grains	5.9 grams
Sodium Carbonate (E. K. Co.)	165 grains	11.3 grams
Potassium Bromide	24 grains	1.7 grams
Cold water to make	32 ounces	1.0 liter

For tray, use 1 part of stock solution to 1 part of water. Develop about 7 minutes at 65° F. (18° C.).

For tank development of roll films, use 1 part of stock solution to 2 parts of water. Develop about 15 minutes at 65° F. (18° C.).

For tank development of professional films, use 1 part of stock solution to 3 parts of water. Develop about 14 minutes at 65° F. (18° C.).

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Two-Solution Contrast Plate Developer [Formula
(Elon-Hydroquinone) D-28]

Stock Solution A

	Avoirdupois	Metric
Water (about 125° F.) (32° C.)	16 ounces	500.0 cc.
Elon	60 grains	4.2 grams
Sodium Sulphite (E. K. Co.)	1½ ounces	45.0 grams
Hydroquinone	120 grains	8.4 grams
Potassium Bromide	50 grains	3.5 grams
Water to make	32 ounces	1.0 liter

Stock Solution B

Water	32 ounces	1.0 liter
Sodium Carbonate (E. K. Co.)	3¼ ounces	97.5 grams

For use, take Stock Solution A, 1 part, Stock Solution B, 1 part. Develop about 4 minutes at 65° F. (18° C.).

Process Tray Developer [Formula
(Hydroquinone-Caustic) D-9]

Stock Solution A

	Avoirdupois	Metric
Water (about 125° F.) (52° C.)	16 ounces	500.0 cc.
Sodium Bisulphite (E. K. Co.)	¾ ounce	22.5 grams
Hydroquinone	¾ ounce	22.5 grams
Potassium Bromide	¾ ounce	22.5 grams
Cold water to make	32 ounces	1.0 liter

Stock Solution B

Cold water	32 ounces	1.0 liter
Sodium Hydroxide (Caustic Soda)	1¾ ounces	52.5 grams

Use equal parts of A and B and develop about three minutes at 65° F. (18° C.).

Cold water should always be used when dissolving sodium hydroxide (caustic soda) because considerable heat is evolved. If hot water is used, the solution will boil with explosive violence and may cause serious burns if the hot alkali spatters on the hands or face. Solution A should be stirred thoroughly when the caustic alkali is added to it; otherwise the heavy caustic solution will sink to the bottom.

Process Tank or Tray Developer [Formula
(Elon-Hydroquinone) D-11]

	Avoirdupois	Metric
Water (about 125° F.) (52° C.)	16 ounces	500.0 cc.
Elon	14 grains	1.0 gram
Sodium Sulphite (E. K. Co.)	2½ ounces	75.0 grams
Hydroquinone	130 grains	9.0 grams
Potassium Carbonate or Sodium Carbonate	360 grains	25.0 grams
Potassium Bromide	70 grains	5.0 grams
Cold water to make	32 ounces	1.0 liter

Formula D-11 used at 65° F. (18° C.), in either tank or tray will give very good contrast in five minutes. The developer is recommended for use with Process and Process Panchromatic Films or Plates.

When less contrast is desired, the developer should be diluted with an equal volume of water.

Tropical Process Developer (Kodolon-Hydroquinone)

[Formula]
D-13

	Avoirdupois	Metric
Water (about 125° F.) (52° C.) . . .	24 ounces	750.0 cc.
Kodolon	75 grains	5.2 grams
Sodium Sulphite (E. K. Co.)	1¾ ounces	52.5 grams
Hydroquinone	150 grains	10.5 grams
Sodium Carbonate (E. K. Co.) . . .	1¾ ounces	52.5 grams
Potassium Iodide	30 grains	2.1 grams
Sodium Sulphate, Crystals	3½ ounces	105.0 grams
Water to make	32 ounces	1.0 liter

Use without dilution. Develop about 6 to 7 minutes at 85° F., or for proportionately longer times at lower temperatures. Rinse for 30 seconds and immerse for 3 minutes in a 5% formalin solution. Then wash for 1 minute, fix in an acid hardening fixing bath (Formula F-1) and wash 15 to 20 minutes.

Tray Developer for Roll Film (Elon-Hydroquinone-Pyro)

[Formula]
D-18a

Stock Solution

	Avoirdupois	Metric
Water (about 125° F.) 52° C.) . . .	16 ounces	500.0 cc.
Elon	20 grains	1.4 grams
Sodium Sulphite (E. K. Co.)	2½ ounces	75.0 grams
Hydroquinone	80 grains	5.6 grams
Sodium Bisulphite (E. K. Co.) . . .	30 grains	2.1 grams
Pyro	½ ounce	15.0 grams
Sodium Carbonate (E. K. Co.) . . .	1½ ounces	45.0 grams
Potassium Bromide	12 grains	0.8 gram
Cold water to make	32 ounces	1.0 liter

For use, take 1 part of stock solution and 1 part of water. Develop 5 to 7 minutes at 65° F. (18° C.).

Long Life Deep Tank Developer for Roll Film (Elon-Hydroquinone-Pyro)

[Formula]
D-75

Solution No. 1

	Avoirdupois	Metric
Water (about 125° F.) (52° C.) . . .	16 ounces	500.0 cc.
Elon	44 grains	3.0 grams

Solution No. 2

	Avoirdupois	Metric
Water (about 125° F.) (52° C.) . . .	16 ounces	500.0 cc.
Sodium Sulphite (E. K. Co.) . . .	260 grains	18.0 grams
Sodium Bisulphite (E. K. Co.) . . .	1¼ ounces	36.0 grams

Solution No. 3

Hot water (about 160° F.) (71° C.) . . .	16 ounces	500.0 cc.
Sodium Sulphite (E. K. Co.) . . .	260 ounces	18.0 grams
Hydroquinone	175 grains	12.0 grams
Pyro	44 grains	3.0 grams

Solution No. 4

Water (about 125° F.) (52° C.) . . .	16 ounces	500.0 cc.
Sodium Carbonate (E. K. Co.) . . .	2½ ounces	72.0 grams

Mix each solution separately and add to the tank in the order given.

Then add water to make 1 gallon 4.0 liters

Develop about 15 minutes at 65° F. (18° C.).

Further details on handling roll films are given in the booklet, "Commercial Photo Finishing."

X-ray Developer
(Elon-Hydroquinone)

[Formula
D-19]

	Avoirdupois	Metric
Water (about 125° F.) (52° C.) . . .	16 ounces	500.0 cc.
Elon	35 grains	2.5 grams
Sodium Sulphite (E. K. Co.) . . .	3½ ounces	105.0 grams
Hydroquinone	140 grains	9.8 grams
Sodium Carbonate (E. K. Co.) . . .	1¾ ounces	52.5 grams
Potassium Bromide	90 grains	6.3 grams
Cold water to make	32 ounces	1.0 liter

Use without dilution. Develop 5 minutes at 65° F. (18° C.).

Motion Picture Developer
Negative or Positive Film

[Formula
D-16]

	Avoirdupois	Metric
Water (about 125° F.) (52° C.) . . .	64 ounces	2.0 liters
Elon	17 grains	1.2 grams
Sodium Sulphite (E. K. Co.) . . .	5¼ ounces	160.0 grams
Hydroquinone	350 grains	24.0 grams
Sodium Carbonate (E. K. Co.) . . .	2½ ounces	75.0 grams
Potassium Bromide	50 grains	3.6 grams
Citric Acid	40 grains	2.8 grams
Potassium Metabisulphite	85 grains	6.0 grams
Cold water to make	1 gallon	4.0 liters

Average time of development 7 to 15 minutes at 65° F. (18° C.).

Negative Motion Picture Developer [Formula] (Elon-Hydroquinone) [D-71]

	Avoirdupois	Metric
Elon	115 grains	8.0 grams
Sodium Sulphite (E. K. Co.)	2½ ounces	75.0 grams
Hydroquinone	29 grains	2.0 grams
Sodium Carbonate (E. K. Co.)	1¾ ounces	50.0 grams
Potassium Bromide	43 grains	3.0 grams
Water to make	1 gallon	4.0 liters

Time of development 6 to 12 minutes at 65° F. (18° C.).

Fine Grain Negative Developer [Formula] For Motion Pictures [D-76] (Elon-Hydroquinone-Borax)

	Avoirdupois	Metric
Elon	115 grains	8.0 grams
Sodium Sulphite (E. K. Co.)	13¼ ounces	400.0 grams
Hydroquinone	290 grains	20.0 grams
Borax	115 grains	8.0 grams
Water to make	1 gallon	4.0 liters

Directions for Mixing: Dissolve the Elon in a small volume of water (at about 125° F.) (52° C.) and add the solution to the tank. Then dissolve approximately one-quarter of the sulphite separately in hot water (at about 160° F.) (71° C.), add the hydroquinone with stirring until completely dissolved. Then add this solution to the tank. Now dissolve the remainder of the sulphite in hot water (about 160° F.) (71° C.), add the borax and when dissolved, pour the entire solution into the tank. Dilute to the required volume with cold water.

Time of development is 10 to 20 minutes at 65° F. (18° C.).

Lantern Slide Formulas

Blue Black Tones [Formula] Stock Solution A [D-34]

	Avoirdupois	Metric
Water (about 125° F.) (52° C.)	16 ounces	500.0 cc.
Elon	60 grains	4.2 grams
Sodium Sulphite (E. K. Co.)	½ ounce	15.0 grams
Hydroquinone	½ ounce	15.0 grams
Cold water to make	32 ounces	1.0 liter

Stock Solution B

Water	32 ounces	1.0 liter
Sodium Carbonate (E. K. Co.)	½ ounce	15.0 grams
Potassium Bromide	30 grains	2.1 grams

For use, take equal parts of A and B.

For softer tones, dilute with an equal quantity of water.

Develop 1½ to 3 minutes at 70° F. (21° C.).

Warm Black Tones [Formula]
Stock Solution A [D-32]

	Avoirdupois	Metric
Water (about 125° F.) (52° C.)	16 ounces	500.0 cc.
Sodium Sulphite (E. K. Co.)	90 grains	6.3 grams
Hydroquinone	100 grains	7.0 grams
Potassium Bromide	50 grains	3.5 grams
Citric Acid	10 grains	0.7 gram
Cold water to make	32 ounces	1.0 liter

Stock Solution B

Cold water	32 ounces	1.0 liter
Sodium Carbonate (E. K. Co.)	1 ounce	30.0 grams
Sodium Hydroxide (Caustic Soda)	60 grains	4.2 grams

For use, take 1 part of A and 1 part of B. For still warmer tones, 1 part of A and 2 parts of B.

Develop about 5 to 6 minutes at 70° F. (21° C.).

Developing Formulas for Paper
Velox, Azo and Bromide Papers [Formula]
Stock Solution [D-72]

	Avoirdupois	Metric
Water (about 125° F.) (52° C.)	16 ounces	500.0 cc.
Elon	45 grains	3.1 grams
Sodium Sulphite (E. K. Co.)	1½ ounces	45.0 grams
Hydroquinone	175 grains	12.2 grams
Sodium Carbonate (E. K. Co.)	2¼ ounces	67.5 grams
Potassium Bromide	27 grains	1.9 grams
Cold water to make	32 ounces	1.0 liter

For use: Dilute 1 to 1 for Velox; 1 to 2 for Azo and 1 to 4 for Bromide Papers.

Develop Velox and Azo 45 seconds at 70° F. (21° C.).

For colder tones on Azo, dilute as for Velox.

Develop Bromide papers 1½ minutes at 70° F. (21° C.).

Acrol Developer for Bromide Papers [Formula]
Stock Solution [D-51]

	Avoirdupois	Metric
Water (about 125° F.) (52° C.)	24 ounces	750.0 cc.
Sodium Sulphite (E. K. Co.)	4 ounces	120.0 grams
Acrol (Diaminophenol Hydrochloride)	1¼ ounces	37.5 grams
Cold water to make	32 ounces	1.0 liter

For use, take 6 ozs. (180 cc.) Stock Solution, ¾ dram (3 cc.) 10% potassium bromide solution, and 24 ozs. (750 cc.) of water. This developer oxidizes quite rapidly when exposed to the air so that only enough developer should be mixed for immediate use.

Portrait Bromide Paper Developer [Formula]
Stock Solution [D-49]

	Avoirdupois	Metric
Water (about 125° F.) (52° C.) . . .	16 ounces	500.0 cc.
Elon	45 grains	3.1 grams
Sodium Sulphite (E. K. Co.)	1½ ounces	45.0 grams
Hydroquinone	165 grains	11.5 grams
Sodium Carbonate (E. K. Co.)	1½ ounces	45.0 grams
Potassium Bromide	30 grains	2.1 grams
Cold water to make	32 ounces	1.0 liter

For use, take Stock Solution, 1 part, water, 1 part. Develop not less than 1½ minutes at 70° F. (21° C.).

Vitava Paper Developer [Formula]
Stock Solution [D-52]

	Avoirdupois	Metric
Water (about 125° F.) (52° C.) . . .	16 ounces	500.0 grams
Elon	22 grains	1.5 grams
Sodium Sulphite (E. K. Co.)	¾ ounce	22.5 grams
Hydroquinone	90 grains	6.3 grams
Sodium Carbonate (E. K. Co.)	½ ounce	15.0 grams
Cold water to make	32 ounces	1.0 liter

For use, dilute as follows:

Vitava Athena—Take Stock Solution, 1 part, water, 1 part. Add ¼ oz. (8 cc.) of 10% potassium bromide solution to each 32 ozs. (1 liter) of developer diluted for use.

Vitava Alba—Use full strength stock solution. Add 1 dram (4 cc.) of 10% potassium bromide solution to each 32 ozs. (1 liter) of developer.

Vitava Rapid Black—Use full strength stock solution. Add ½ oz. (16 cc.) of 10% potassium bromide solution to each 32 ozs. (1 liter) of developer.

Vitava Zelta—Take Stock Solution, 1 part, water, 1 part. Add ½ oz. (16 cc.) of 10% potassium bromide solution to each 32 ozs. (1 liter) of developer diluted for use.

Develop not less than 1½ minutes at 70° F. (21° C.).

Additional formulas are to be found in "Book of Formulas for Eastman Papers," published by the Eastman Kodak Company, Rochester, N. Y.

RINSE BATHS

Acid Rinse Bath for Paper [Formula SB-1]

After development, rinse prints thoroughly in running water or in the following acid rinse bath before placing in the fixing bath (Formula F-1).

	Avoirdupois	Metric
Water	32 ounces	1.0 liter
*Acetic Acid (28% pure) (E. K. Co.)	1½ ounces	48.0 cc.

*To make 28% acetic acid from glacial acetic acid dilute three parts of glacial acid with eight parts of water.

Chrome Alum Hardening Bath [Formula SB-3] for Films and Plates

In hot weather, the following hardening bath should be used after development and before fixation in conjunction with Formula F-1 or when F-16 does not harden sufficiently.

	Avoirdupois	Metric
Water	32 ounces	1.0 liter
Potassium Chrome Alum	1 ounce	30.0 grams

Agitate the negatives for a few seconds when first immersed in hardener. This bath should be renewed frequently.

FIXING BATHS

Acid Hardening Fixing Bath for [Formula F-1] Films, Plates and Papers

	Avoirdupois	Metric
Hypo	16 ounces	480.0 grams
Water to make	64 ounces	2.0 liters

Then add the following hardener solution slowly to the cool hypo solution while stirring the latter rapidly.

Water (about 125° F.) (52° C.)	5 ounces	160.0 cc.
Sodium Sulphite (E. K. Co.)	1 ounce	30.0 grams
*Acetic Acid (28% pure) (E. K. Co.)	3 ounces	96.0 cc.
Powdered Potassium Alum	1 ounce	30.0 grams

Dissolve in the order given.

If it is desired to mix a stock hardener solution, use:

Acid Hardener Stock Solution [Formula F-1a]

	Avoirdupois	Metric
Water (about 125° F.) (52° C.)	56 ounces	1700.0 cc.
Sodium Sulphite (E. K. Co.)	16 ounces	480.0 grams
*Acetic Acid (28% pure) (E. K. Co.)	48 ounces	1500.0 cc.
Powdered Potassium Alum	16 ounces	480.0 grams
Cold water to make	1 gallon	4.0 liters

*To make 28% acetic acid from glacial acetic acid, dilute three parts of glacial acid with eight parts of water.

For use, add 1 part of cool stock solution slowly with stirring, to 8 parts of a 25% cool hypo solution.

To make up the hardener dissolve the chemicals in the order given above. The sodium sulphite should be dissolved completely before adding the acetic acid. After the sulphite-acid solution has been mixed thoroughly, add the potassium alum with constant stirring. If the hypo is not thoroughly dissolved before adding the hardener a precipitate of sulphur is likely to form.

Chrome Alum Fixing Bath for [Formula] Films and Plates F-16

Solution A

	Avoirdupois	Metric
Hypo	2 pounds	960.0 grams
Sodium Sulphite (E. K. Co.)	2 ounces	60.0 grams
Water to make	96 ounces	3.0 liters

Solution B

Water	32 ounces	1.0 liter
Potassium Chrome Alum	2 ounces	60.0 grams
Sulphuric Acid, pure concentrated	1/4 ounce	8.0 cc.

Pour B solution into A solution slowly while stirring A rapidly. This formula is especially recommended for use in hot weather but it loses its hardening properties in a few days either with or without use and therefore should be used as soon as possible after mixing.

Motion Picture Fixing Bath [Formula] F-2

	Avoirdupois	Metric
Water	1 gallon	4.0 liters
Hypo	2 pounds	960.0 grams

When thoroughly dissolved, add the following cool hardener solution slowly with stirring to the cool hypo solution.

Water	4 ounces	128.0 cc.
Sodium Sulphite (E. K. Co.)	175 grains	12.0 grams
*Acetic Acid (28% pure) (E. K. Co.)	2 1/4 ounces	72.0 cc.
Powdered Potassium Alum	350 grains	24.0 grams

Dissolve in the order given following the directions for mixing the stock hardener (Formula F-1a) given on page 55.

Deep Tank Fixing Bath for Roll Films [Formula] F-14

	Avoirdupois	Metric
Water	1 gallon	4.0 liters
Hypo	2 pounds	960.0 grams

When thoroughly dissolved, add the following cool hardener slowly with constant stirring to the cool hypo solution.

	Avoirdupois	Metric
Water	13 ounces	400.0 cc.
Sodium Sulphite (E.K. Co.)	1 ounce	30.0 grams
*Acetic Acid (28% pure) (E. K. Co.)	6½ ounces	208.0 cc.
Powdered Potassium Alum	2 ounces	60.0 grams

*To make 28% acetic acid from glacial acetic, take 3 parts of glacial acid and add 8 parts of water.

Dissolve in the order given following the directions for mixing the stock hardener (Formula F-1a) given on page 55.

Hypo Test Solution

[Formula
HE-1]

	Avoirdupois	Metric
Potassium Permanganate	4 grains	0.3 gram
Sodium Hydroxide (Caustic Soda)	8 grains	0.6 gram
Water (distilled) to make	8 ounces	250.0 cc.

Take 8 ounces (250 cc.) of pure water in a clear glass and add ¼ dram (1 cc.) of the Hypo Test Solution. A film, or two or three prints should then be taken from the wash water and allowed to drip into the glass containing the Hypo Test Solution.

If a small percentage of hypo is present the violet color will turn green, and with larger concentrations of hypo the green color will change to deep yellow. In either case the film or prints should be returned to films or the wash water and allowed to remain until further tests prove that the hypo has been eliminated. This is shown by the violet color remaining unchanged when drippings are added to the glass containing the Hypo Test Solution.

REDUCERS

Persulphate Reducer Stock Solution

[Formula
R-1]

	Avoirdupois	Metric
Water	32 ounces	1.0 liter
Ammonium Persulphate	2 ounces	60.0 grams
Sulphuric Acid C. P.	¾ dram	3.0 cc.

For use, take one part of stock solution and two parts of water.

When reduction is complete, immerse in an acid fixing bath for a few minutes, then wash.

Permanganate Reducer Stock Solution A

[Formula
R-2]

	Avoirdupois	Metric
Water	32 ounces	1.0 liter
Potassium Permanganate	1¾ ounces	52.5 grams

Stock Solution B

Cold water	32 ounces	1.0 liter
Sulphuric Acid C. P.	1 ounce	32.0 cc.

For use, take stock solution A, 1 part, stock solution B, 2 parts, water 64 parts. When the negative has been sufficiently reduced, immerse in a plain hypo solution, or in a fresh acid fixing bath for a few minutes, to remove yellow stain, after which wash thoroughly.

The best method of dissolving the permanganate crystals in Solution A is to use a small volume of hot water (about 180° F.) (82° C.) and shake or stir the solution vigorously until completely dissolved; then dilute to volume with cold water. When preparing Stock Solution B, *always add the sulphuric acid to the water slowly with stirring and never the water to the acid*, otherwise the solution may boil and spatter the acid on the hands or face causing serious burns.

Farmer's Reducer Solution A

[Formula
R-4]

	Avoirdupois	Metric
Potassium Ferricyanide	15 grains	1.0 gram
Water	1 ounce	32.0 cc.

Solution B

Hypo	1 ounce	30.0 grams
Water	32 ounces	1.0 liter

Add A to B and immediately pour over the negative to be reduced. The formula should be prepared immediately before using as it decomposes rapidly after mixing together the A and B solutions. When the negative has been reduced sufficiently, wash thoroughly before drying.

Proportional Reducer Stock Solution A

[Formula
R-5]

	Avoirdupois	Metric
Water	32 ounces	1.0 liter
Potassium Permanganate	4 grains	0.3 gram
Sulphuric Acid (10% solution)	½ ounce	16.0 cc.

Stock Solution B

Water	96 ounces	3.0 liters
Ammonium Persulphate	3 ounces	90.0 grams

For use, take one part of A to three parts of B. When sufficient reduction is secured the negative should be cleared in a 1% solution of sodium bisulphite. Wash the negative thoroughly before drying.

INTENSIFIERS

Mercury Intensifier (Monckhoven)

[Formula
In-1]

Bleach the negative in the following solution until it is white, then wash thoroughly:

	Avoirdupois	Metric
Potassium Bromide	¾ ounce	22.5 grams
Mercuric Chloride	¾ ounce	22.5 grams
Water to make	32 ounces	1.0 liter

The negative can be blackened with 10% sulphite solution, a developing solution, such as (Formula D-72) diluted 1 to 2, or 10% ammonia, these giving progressively greater density in the order given. To increase contrast greatly, treat with the following solution:

	Avoirdupois	Metric
Sodium or Potassium Cyanide	½ ounce	15.0 grams
Silver Nitrate	¾ ounce	22.5 grams
Water to make	32 ounces	1.0 liter

Dissolve the cyanide and silver nitrate separately, and add the latter to the former, until a permanent precipitate is just produced; allow the mixture to stand a short time and then filter. This is called *Monckhoven's Intensifier*.

Chromium Intensifier Stock Solution

[Formula
In-4]

	Avoirdupois	Metric
Potassium Bichromate	3 ounces	90.0 grams
Hydrochloric Acid, concentrated	2 ounces	64.0 cc.
Water to make	32 ounces	1.0 liter

For use, take 1 part of stock solution to 10 parts of water. Bleach thoroughly, then wash five minutes and re-develop in either Nepera Solution 1:4 or in the Elon Hydroquinone developer (Formula D-72) diluted 1:2. Then wash thoroughly. Greater intensification can be secured by repeating the process.

Re-Development Intensifier

Perhaps the simplest method of intensification for negatives consists of bleaching in the ferricyanide and bromide formula used for the sepia toning of prints (Formula T-7a page 60) and then blackening with sodium sulphide exactly as in print toning.

TONING FORMULAS

Sepia Toning—Hypo-Alum Bath [Formula T-1a]

	Avoirdupois	Metric
Cold water	90 ounces	2800.0 cc.
Hypo	16 ounces	480.0 grams

Dissolve thoroughly, and add the following solution:

Hot water (about 160° F.) (71° C.)	20 ounces	640.0 cc.
Powdered Potassium Alum	4 ounces	120.0 grams

Then add the following solution (including precipitate) *slowly to the hypo-alum solution while stirring the latter rapidly.*

Cold water	2 ounces	64.0 cc.
Silver Nitrate Crystals	60 grains	4.2 grams
Sodium Chloride (Table Salt)	60 grains	4.2 grams

After combining above solutions,

Add water to make	1 gallon	4.0 liters
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Note: The silver nitrate should be dissolved completely before adding the sodium chloride and immediately afterward, the solution containing the milky white precipitate should be added to the hypo-alum solution as directed above. The solution should be milky white if correctly mixed.

For use, pour into a tray standing in a water bath and heat to 120° F. (49° C.). Prints will tone in 12 to 15 minutes. If boiling water is used, for mixing the toning bath, or if the order of mixing is changed or if the hypo-alum bath is not stirred when adding the white precipitate, the bath will turn a dirty gray or black. The bath should never be heated higher than 130° F. (54° C.) otherwise blistering, staining and non-uniform toning will result.

Re-Developing Stock Solution [Formula T-7a]

No. 1—Stock Bleaching Solution

	Avoirdupois	Metric
Potassium Ferricyanide	2½ ounces	75.0 grams
Potassium Bromide	2½ ounces	75.0 grams
Potassium Oxalate	6½ ounces	195.0 grams
Acetic Acid (28% pure)	1¼ ounces	40.0 cc.
Water	64 ounces	2.0 liters

No. 2—Stock Re-Developing Solution

Sodium Sulphide (not Sulphite)	1½ ounces	45.0 grams
Water	16 ounces	500.0 cc.

Prepare Bleaching Bath as follows:

Stock Solution No. 1	16 ounces	500.0 cc.
Water	16 ounces	500.0 cc.

Prepare Re-Developer as follows:

	Avoirdupois	Metric
Stock Solution No. 2	4 ounces	130.0 cc.
Water	32 ounces	1.0 liter

Working Directions: Immerse print, which should first be washed thoroughly, in the Bleaching Bath, allowing it to remain until only faint traces of the half-tones are left and the black of the shadows has disappeared. This operation will take about one minute.

Note: Particular care should be taken *not* to use trays with any *iron* exposed, otherwise blue spots may result.

Rinse *thoroughly* in clean cold water as all chemicals must be removed.

Place in Re-Developer Solution until original detail returns (for about thirty seconds). Immediately after the print leaves the Re-Developer, rinse *thoroughly*, then immerse it for five minutes in a hardening bath composed of 1 part of the hardener recommended for the acid fixing bath (Formula F-1a) (page 55) and 16 parts of water. Remove the print from this bath and wash for one-half hour in running water. The color and gradation of the finished print will not be affected by the use of this bath.

Stain Remover

[Formula
S-6]

Developer or oxidation stain may be removed by first hardening the film for 2 or 3 minutes in a 5% formalin solution, then washing for 5 minutes and bleaching in:

Stock Solution A

	Avoirdupois	Metric
Potassium Permanganate	75 grains	5.3 grams
Water to make	32 ounces	1.0 liter

Stock Solution B

Sodium Chloride (Table Salt)	2½ ounces	75.0 grams
Sulphuric Acid, pure concentrated	½ ounce	16.0 cc.
Water to make	32 ounces	1.0 liter

Use equal parts of A and B. The solutions should not be mixed until ready for immediate use since they do not keep long after mixing. All particles of permanganate should be dissolved completely when preparing Solution A (see hint on dissolving permanganate, page 58), since undissolved particles are likely to produce spots on the negative. Bleaching should be complete in 3 or 4 minutes. The brown stain resulting from manganese dioxide is best removed by immersing the negative in 1% sodium bisulphite solution. Then rinse well and develop in strong light (not sunlight) with any ordinary developer such as Formula D-72 diluted 1 part to 2 parts of water (see page 53).

CHAPTER IX.

Preparing Solutions

A solution of any kind is obtained by dissolving a solid or a liquid in another liquid (or solid). The substance being dissolved is called the solute and the liquid in which it is dissolved is called the solvent. The extent to which the solute is soluble in the solvent is called its solubility and when the solvent will hold no more of the solute it is said to be saturated.

The degree of solubility of any chemical depends on the nature of the solvent and on the temperature, which should always be stated.

If a saturated solution is cooled to a lower temperature, crystals usually form which settle out until the saturation point is reached at that particular temperature, though in the case of a substance like hypo, if all dust is excluded, crystals do not separate out on cooling and a so-called super-saturated solution is obtained. However, if a small crystal of hypo is added to the solution, crystals immediately form and continue to grow until the saturation point is reached. The best method of preparing a saturated solution, therefore, is to dissolve the chemical in hot water, cool to room temperature with shaking, allow to stand, and filter.

For photographic work, saturated solutions are not recommended because of their unreliability relative to the concentration of the chemicals used. Solutions of definite percentage strength are to be preferred and are always specified in Eastman formulas.

When a chemical is dissolved in water the volume of the solution is usually greater than that of the water, because the particles or molecules of the chemical occupy a certain space when in solution. In case two liquids are mixed, the final volume of the liquid is not necessarily equal to the sum of the volumes of the liquids mixed; it may be greater or it may be less. Thus fifty volumes of alcohol when added to fifty volumes of water at 70° F., produce ninety-seven volumes of the mixture and not one hundred. Moreover, equal weights of different chemicals do not occupy the same volume.

In photography we are concerned only with the weight or volume of each chemical in a fixed volume of the solution, so

that when mixing, the chemical should be dissolved in a volume of water appreciably less than that called for in the formula and then water added *up to* the volume stated.

When mixing photographic solutions, the importance of following manufacturers' instructions issued with formulas cannot be over estimated. The quantities and the order of ingredients have been established by extensive tests and to change them is very apt to affect the useful properties of the solutions.

Weights and Measures

In photographic practice, solids are weighed and liquids are measured either by the Avoirdupois or the Metric system.

The following tables of weights and measures give all the equivalent values required for converting photographic formulas:

Weights and Measures—Conversion Tables

Avoirdupois to Metric Weight

Pounds	Ounces	Grains	Grams	Kilograms
1	16	7000	453.59	0.45359
0.0625	1	437.5	28.35	0.02835
		1	0.0647	
	0.03527	15.432	1	0.001
2.2046	35.274	15432	1000	1

U. S. Liquid to Metric Measure

Gallons	Quarts	Fluid Ounces	Fluid Drams	Cubic Centimeters	Liters
1	4	128	1024	3785.3	3.785
0.25	1	32	256	946.3	0.9463
		1	8	29.6	0.0296
0.001	0.004	0.125	1 (60 mins.)	3.696	0.0037
		0.0338	0.271	1	0.001
0.264	1.056	33.8	270.52	1000	1

When a formula is expressed in grains, ounces, and pounds, it may be converted into a metric formula by using the following conversion values which take into account the difference between 32 ounces and one liter. After a conversion has been made, the values obtained should be rounded off to give convenient working quantities. The error introduced in rounding off a value should not be greater than 5 per cent and the ratio between chemicals such as Elon and hydroquinone, or carbonate and sulphite should not be changed.

Solid Conversion Values

Grains per 32 ozs. multiplied by	0.06834	= grams per liter
Ounces per 32 ozs. multiplied by	29.924	= grams per liter
Pounds per 32 ozs. multiplied by	478.8	= grams per liter
Grams per liter multiplied by	14.6	= grains per 32 ozs.
Grams per liter multiplied by	0.03335	= ounces per 32 ozs.
Grams per liter multiplied by	0.002085	= pounds per 32 ozs.

Liquid Conversion Values

Ounces (liquid) per 32 ozs. multiplied by	31.22	= cubic centimeters per liter
Quarts per 32 ozs. multiplied by	1000	= cubic centimeters per liter
Cubic centimeters per liter multiplied by	0.032	= ounces (liquid) per 32 ozs.
Cubic centimeters per liter multiplied by	0.001	= ounces (liquid) per 32 ozs.

Thus a developer formula for a 42 gallon tank would be converted as follows:

Formula

Water	5 gallons	
Elon	1 ounce	25 grains
Sodium Sulphite	52 ounces	
Potassium Metabisulphite	1 ounce	272 grains
Hydroquinone	4 ounces	86 grains
Pyro	10 ounces	
Sodium Carbonate	27 ounces	358 grains
Potassium Bromide		260 grains
Add water to make	42 gallons	

Conversion

	Direct	Rounded-off
Water	20.0 liters	20 liters
Elon	31.5 grams	32 grams
Sodium Sulphite	1556.1 grams	1560 grams
Potassium Metabisulphite	48.5 grams	49 grams
Hydroquinone	125.6 grams	126 grams
Pyro	299.2 grams	300 grams
Sodium Carbonate	831.4 grams	835 grams
Potassium Bromide	17.8 grams	18 grams
Add water to make	168.0 liters	168 liters

To convert a metric formula into an avoirdupois formula, the process should be reversed using the values given in the second part of the foregoing conversion table. Values in grains should be rounded off to the nearest quarter ounce, whenever it is possible to do so without introducing an error greater than 5 per cent.

It is often recommended to dissolve, say, 10 parts of a solid in 100 parts of water. In the case of liquids, parts should be taken as meaning units of volume and in the case of solids as units of weight. A "part" may, therefore, mean anything from a grain to a ton, or a minim to a gallon so long as the other quantities are reckoned in the same units of weight or volume.

Thus:

For use, take		For use, take		
Solution A.	3 parts	} may mean {	Solution A.	15 ozs.
Solution B.	1 part		Solution B.	5 ozs.

If the formula contains both solids and liquids, if ounces (liquid) and ounces (solid) are substituted for "parts," the error involved falls within permissible limits.

Example:

Mix one gallon of solution according to the following formula:

Sodium Sulphite	10 parts
Pyro	1 part
Water to make	100 parts

One gallon equals 128 ozs. Therefore, dissolve $10 \times 128 \div 100 = 12 \frac{4}{5}$ ozs. of sulphite in water, add $1 \frac{1}{4}$ ozs. of Pyro, and make up to 1 gallon.

When quantities of chemicals under 10 grains or 0.7 gram are included in a formula, they are expressed preferably as a 10 per cent solution to be added as so many drams or cc. If less than a dram is required, an even quarter fraction thereof ought to be used. This plan avoids expressing the volume in "drops," which is a very uncertain quantity varying as much as 150 per cent depending on the way it is measured and the specific gravity of the liquid used. The average drop from the usual dropping bottle or burette measures about one minim or less than one-tenth of a cc.

Many photographers are accustomed to making up their stock solutions of hypo, carbonate, sulphite, etc., by means of the hydrometer. This method has the advantage that in case the chemical has become moist and contains an unknown quantity of water, a definite reading on the hydrometer will give a solution of the same strength as if perfectly dry chemicals had been used. When a stock solution is made from moist chemicals by weighing, the error caused by the presence of water may be as high as 25% or 50%.

The hydrometer method has the disadvantage that the adjustment of a solution to the required strength takes considerable time, it does not convey any idea as to the percentage strength of the solution, and varies with the temperature. For instance, if a stock solution is made with hot water and this registers, say, 45 on the hydrometer, on cooling, the liquid may register 48 or 50. It is therefore absolutely

necessary either to make all readings when the solutions have cooled to room temperature, or to prepare a table giving the variation of density of each solution with temperature.

Mixing stock solutions by hydrometer test is not recommended because it is much simpler to compound these by weighing. A subsequent hydrometer reading, however, is sometimes a rough check that the solution has been mixed correctly. *A hydrometer test of a mixed developer or fixing bath has no meaning whatever.* The only way to test a photographic solution is actually to process therein the photographic material for which it was intended.

Stock Solutions

A stock solution is a concentrated solution to which water is added before use.

The limiting strength of solution which it is possible to make in any particular case depends on the solubility of the chemical, and as the solubility diminishes with temperature, a solution should not be made stronger than a saturated solution at 40°F., (4.4°C) otherwise, in cold weather, the substance would crystallize out.

A stock solution of sodium sulphite should be made as strong as possible (20% of the desiccated salt) because at such a strength the solution oxidizes very slowly and will therefore keep, whereas in weaker solution, it combines with the oxygen in the air very readily and is then useless as a preservative.

Percentage Solutions

The percentage strength of a photographic solution indicates the quantity of the chemical which is dissolved in 100 ounces or 100 cc. of the solution. A percentage solution is prepared by dissolving the specified quantity of the chemical in a small volume of water and adding water to make 100 ounces (or 100 cc.). In the avoirdupois system a 10% solution of a solid is made by taking one ounce and making up to ten ounces with water. Converting these figures into grams and cc. we have, roughly, 30 grams in 300 cc. or a 10% solution.

A 10% solution of a liquid in water is made by taking 10 ounces or 10 cc. of the liquid and adding water to make 100 ounces or 100 cc. respectively.

The great advantage of stating the strength of any solution in parts per hundred is that a definite mental picture is at once created of its relative strength, while by means of a

number of stock solutions it is possible to compound certain formulas by simply measuring out a definite volume of each solution thus dispensing with a balance. Thus supposing we have 10% solutions of potassium ferricyanide and of potassium bromide already at hand and it is desired to make up the following solution:

Potassium Ferricyanide	6 grams
Potassium Bromide	2.3 grams
Water to	1000 cc.

then it is only necessary to measure out 60 cc. of the ferricyanide solution, 23 cc. of the bromide solution, and add water to make 1000 cc.

Suppose a formula calls for 0.1 gram. It is impossible to weigh this quantity accurately on the usual photographic scale, but by measuring out 10 cc. of a 1% solution, and adding this to the mixture the problem is solved.

Terminology and Arrangement of Formulas

In the publication of formulas it is convenient from several standpoints to adopt a standard volume of solution for tray and tank work. Eastman formulas are published, therefore, on a 32 ounce or 1 liter basis or quarter fraction thereof for tray purposes, and a 1 gallon or 4 liters or quarter fraction thereof for tank purposes. For special purposes such as motion picture or photo finishing work it is necessary to use larger volumes for tank formulas.

As a general rule in published formulas the term "Cold water to make" is always given at the end of the formula. This insures dilution to a definite volume, thus yielding a known concentration of chemicals each time the formula is mixed. With many developers a volume of water at about 125° F. (52° C.) is given at the beginning of the formula, sufficient to dissolve all the chemicals. When finally diluted to volume with cold water, the solution will usually be at a satisfactory working temperature, 65° to 70° F. (18° to 21° C.).

The term "Stock Solution" should precede every formula which needs to be diluted for use. As mentioned previously, the order of chemicals in a formula is established carefully and should always be followed when preparing a solution.

Names of chemicals used in Eastman formulas are those accepted by standard text books of chemistry. Vague or inaccurate terms such as sulphuret of hydrogen, soda crystals, liver of sulphur, etc., are eliminated.

Apparatus

For quantities up to four pounds or 2000 grams a double pan balance should be used. For still larger quantities a platform scale may be used. For preparing small quantities of sample developers a small chemical balance weighing to one-tenth of a grain or one-hundredth gram is necessary.

For small quantities of solution conical glass flasks are the most suitable, for larger quantities enameled buckets. Earthenware crocks are usually unsatisfactory because when the glaze cracks, the solutions penetrate the pores and thus contaminate any other solutions subsequently mixed in them.

A wooden stick or paddle made of spruce or cypress is the best form of stirrer, but a separate one should be used for each solution to eliminate the possibility of contamination. Paddles should be wax impregnated by first soaking in water for several hours to open the pores, and then immersing in hot paraffin wax which displaces the water. The wax solution should be kept very hot so that only a thin surface layer of wax is retained when the paddle is withdrawn.

The paddle may also be used to measure out a definite volume of solution in a tank or crock by marking it to correspond with definite volumes when held vertically. Such markings are only applicable, however, to the particular tank or crock for which the paddle was graduated, so that a separate paddle should be used for each tank or crock unless they are of the same shape and capacity.

Materials for making containers for photographic solutions vary according to the nature and volume of the solutions to be used. Trays and small tanks are usually satisfactory if made from any of the following: glass, (such as Pyrex) enameled steel, reinforced hard rubber, wax impregnated wood (cypress or spruce), wood lined with a good grade of sheet rubber or rubberized cloth, well glazed porcelain, or laminated phenolic condensation products.

Large tanks, vats, and drums should be made of hard glazed stoneware, Alberene stone, wax impregnated spruce or cypress, or wood lined with chemical lead and "burned" seams. Another simple inexpensive method of tank construction is to flow hot "Oxygenated" asphalt over the surface of a cypress wood tank. The asphalt should not contain phenolic products or chemical fog will be produced in developer solutions.

Tin, copper, and zinc, or alloys of these metals will usually produce bad fog and stain with photographic developers, and are also unsatisfactory for use in fixing baths.

Mixing Operations

Chemicals should be weighed and solutions prepared outside the darkroom. Care must be taken when handling such substances as hydroquinone, resublimed pyro, potassium ferricyanide, etc., not to shake the finer particles into the air, otherwise they will enter the ventilating system and settle on benches, negatives and prints, thus causing no end of trouble in the way of spots and stains.

Weigh chemicals on pieces of paper and after transferring to the mixing vessel do not shake the paper but lay it in the sink and allow water to flow over it, thus dissolving the dust. Larger quantities are most conveniently weighed in buckets.

For small volumes of solutions a glass graduate marked off in ounces should be used; for larger volumes use a bucket previously graduated, or mark off the inside of the tank or crock used for mixing. When measuring a liquid in a glass graduate, place the eye on a level with the graduation mark and pour in the liquid until its lower surface coincides with this level. Owing to capillary attraction the liquid in contact with the walls of the graduate is drawn up the sides, so that on viewing sideways it appears as if the liquid has two surfaces. All readings should be made from the lower surface and at room temperature because a warm liquid contracts on cooling.

The rapidity with which a substance dissolves in any solvent depends on its solubility and degree of fineness, the temperature of the solvent, and the rate of stirring. Since a chemical is usually more soluble in hot water than in cold, the quickest way of mixing a solution is to powder it and dissolve in hot water with stirring. In the case of a few substances like common salt, which are only slightly more soluble in hot than in cold water, the use of hot water is of no advantage.

Since most solutions are intended for use at ordinary temperatures (65° to 70° F.) (18° to 21° C.), if hot water is used for dissolving, the solution must be cooled again if it is required for immediate use, though usually the time taken to do this is less than the extra time which would be taken up in dissolving the chemicals in cold water. When mixing,

therefore, as a general rule, dissolve the chemical in as small a volume of hot water as possible, cool and dilute with cold water.

After diluting with water, thoroughly shake the solution if in a bottle, or stir if in a tank, otherwise the water added will simply float on top of the heavier solution.

When mixing a solution in a tank, never put the dry chemicals into the tank, but always make sure that they are dissolved by mixing in separate buckets and filtering into the tank.

In the case of anhydrous (dry) salts, such as desiccated sodium carbonate, sodium sulphite, *always add the chemical to the water and not vice versa, otherwise a hard cake will form which will dissolve only with difficulty.*

It is necessary to remove from the solution any suspended matter such as dirt, caused by the presence of dust in the chemicals used, and also any residue or undissolved particles which might settle on the film, plates or paper during development.

A combination of methods for removing such particles is the best and most desirable as follows:

(a) For volume of solution up to five gallons, filter through a fine cloth into a bottle or crock fitted with a side tube and pinch cock or screw clamp. In this way the fine particles settle but the drainage tube is sufficiently high so as not to disturb the sediment. The cloth or muslin should be washed thoroughly, otherwise the sizing matter in the fabric will be washed into the solution and settle as a sludge.

(b) For large volumes of solutions such as are used in photo finishing work, the best arrangement for mixing is to place the chemical room immediately above the developing room, and to mix the solutions in large wooden vats, stone-ware or enameled tanks connected with the lead piping to the developing and fixing tanks in the darkroom below. The solutions can then be mixed in advance, allowed to settle, and tested, so that only correct solutions pass into the tanks.

When mixing large volumes of solution in a tank, stretch a cloth filter bag over the tank, place the chemicals in the bag and allow hot water to flow into it. In this way the chemicals are dissolved and the solution filtered at the same time. A separate bag should be used for each solution to eliminate all risk of contamination.

Finely divided chemicals should be dissolved separately in enameled pails, using a small volume of warm water (about 125° F.) (52° C.), and then filtered by pouring into the filter bag.

The settling of a semi-colloidal sludge can usually be hastened by mixing the solution in warm water, because the warmth tends to coagulate the suspension and cause the particles to cluster together. Thus if crystals of sodium sulphide which are brown, due to the presence of iron, are dissolved in warm water the colloidal iron sulphide coagulates and settles out rapidly, leaving a perfectly colorless solution.

When mixing chemicals, if the solution is not filtered or if a coarse filter is used, a scum usually rises to the surface consisting of fibers, dust, etc., which should be skimmed off with a towel.

When a fixing bath has been used for some time and is allowed to stand undisturbed for a few days, any hydrogen sulphide gas which may be present in the atmosphere forms a metallic looking scum of silver sulphide at the surface of the liquid, and on immersing the film this scum attaches itself to the gelatin and prevents the action of the fixing bath. Any such scum should be carefully removed before use, with a sheet of blotting paper or by using a skimmer made of several layers of cheese cloth stretched on a frame.

The Water Supply in Photographic Operations

Water is the most widely used chemical in photography and it is important therefore to know to what extent the impurities in it may be harmful to the various photographic operations and how these impurities may be removed.

Impurities in Water. Excluding distilled water, rain water, and water from clean melted ice or snow, impurities may be present as follows:

1. Dissolved salts such as bicarbonates, chlorides, and sulphates of calcium, magnesium, sodium, and potassium.

2. Suspended matter which may consist of:

A. Mineral matter such as mud, iron rust, or free sulphur.

B. Vegetable matter such as decayed vegetation.

C. Animal matter such as biological growths and bacteria.

The suspended particles may be of colloidal dimensions when they are difficult to remove by filtration.

3. Dissolved extracts usually colored yellow or brown from decayed vegetable matter and the bark of trees.

4. Dissolved gases such as air, carbon dioxide, and hydrogen sulphide.

Impurities in the water supply are not responsible, however, for as many troubles as is usually supposed. If developing solutions are mixed with warm water (about 125°F.) (52° C.) and allowed to stand over night, any precipitate or suspended matter will settle and the clear supernatant liquid may be drawn off for use. The presence of calcium and other salts is sometimes beneficial as they tend to retard the swelling of the gelatin coating of films, plates, and papers during washing. This is of particular advantage in hot weather.

The only impurities liable to cause serious trouble with developers are hydrogen sulphide or soluble metallic sulphides. With such water about 25 grains of lead acetate per gallon (0.4 gram per liter) of developer should be added before mixing. This removes the sulphides, as lead sulphide and any excess lead is precipitated in the developer and settles on standing.

No trouble may be anticipated with fixing baths prepared with average samples of impure water providing the bath is clarified by settling before use.

When washing photographic materials little trouble may be anticipated with uncolored water if the following precautions are taken: (a) remove all suspended matter by filtering, either by means of commercial filters or by placing two or three layers of cloth over the water outlet; (b) remove thoroughly all excess moisture from the films, plates or paper before drying.

Water which even after filtering is colored brown is very apt to cause staining of the highlights of paper prints. It is a difficult matter to remove economically the coloring matter from such waters and each case usually requires specific treatment.

Further information on the water supply is contained in a pamphlet on that subject obtainable on request from the Service Department, Eastman Kodak Co., Rochester, N.Y.

How to Mix Developing Solutions

A developer usually contains four ingredients as follows:

1. *The developing agent* (Elon, hydroquinone, pyro, para-aminophenol, etc.).
2. *The alkali* (carbonates and hydroxides of sodium, potassium, lithium and ammonium).
3. *The preservative* (sulphites, bisulphites, and meta-bisulphites of sodium and potassium).
4. *The restrainer* (bromides and iodides of sodium and potassium).

If a developing agent like hydroquinone is dissolved in water, the solution will either not develop at all or only very slowly, and on standing it will gradually turn brown, because of what is called oxidation or chemical combination of the hydroquinone with the oxygen present in the air in contact with the surface of the liquid. This oxidation product is of the nature of a dye and will stain fabrics or gelatin just like a dye solution.

On adding a solution of an alkali such as sodium carbonate, the hydroquinone at once becomes a developer, but at the same time the rate of oxidation is increased to such an extent that the solution very rapidly turns dark brown, and if a plate is developed in this solution it becomes stained and fogged.

If we add a little sodium bisulphite to the brown colored solution mentioned above, the brown color or stain is bleached out and a colorless solution is obtained. Therefore, if the preservative is first added to the developer, on adding the accelerator the solution remains perfectly clear because the sulphite preserves or protects the developing agent from oxidation by the air.

As a general rule, therefore, the preservative should be dissolved first.

An exception to this rule should be observed with concentrated formulas containing the developing agents, Elon, or Roylon. These substances are readily soluble in warm water (about 125° F.) (52° C.) and do not oxidize rapidly. If the sulphite is dissolved before the Elon, as is the case with developers such as hydroquinone, a white precipitate often appears especially if the sulphite solution is concentrated. This precipitate forms because Elon is a combination of an insoluble base with an acid which renders it soluble. When the acid portion is neutralized by a weak alkali such as so-

dium sulphite, the insoluble base is precipitated. This Elon precipitate is soluble in an excess of water and also in a sodium carbonate solution with which the base forms a soluble sodium salt. When once the Elon is dissolved, however, it takes a fairly high concentration of sulphite to bring it out of solution again, though only a low concentration of sulphite is required to prevent the Elon from dissolving. If a precipitate forms on dissolving the Elon and sulphite, this will usually redissolve on adding the carbonate and no harm has been done.

Some direction sheets recommend that a portion of the sulphite should be dissolved in order to prevent the oxidation of the Elon, then dissolve the Elon, and then the remainder of the sulphite. Many workers add a little of the solid sulphite to the Elon when dissolving the latter. This procedure is quite satisfactory, though if the Elon is dissolved alone in water at a temperature not above 125° F. (52° C.), and the sulphite dissolved immediately afterwards, little or no oxidation products will be formed which would otherwise produce chemical stain.

The alkali (usually carbonate) may be added in one of three ways:

(a) Dissolve the carbonate separately and add to the cooled Elon-sulphite solution. There is danger, however, of the Elon precipitating before the carbonate is added.

(b) Add the solid carbonate to the Elon-sulphite solution, stirring thoroughly until dissolved.

(c) After dissolving the Elon, dissolve the sulphite and carbonate together, cool and add to the Elon-solution.

Bromides and iodides are added to a developer to compensate for any chemical fog produced by the developer, or inherent in the emulsion. It is immaterial at what stage the bromide is added during the mixing.

When mixing a developer the following rules should, therefore, be followed:

1. *Dissolve the chemicals in the order given unless the mixing directions specify changes in the order of solution.* If a formula contains both sulphite and bisulphite, it is usual to dissolve these together, that is the bisulphite is dissolved in the same order as the sulphite.

2. *Dissolve each chemical completely before adding the next.* If the alkali is added before the crystals of the developing

agent are dissolved, each crystal becomes oxidized at the surface and the resulting solution will give fog.

3. *Mix the developer at the temperature recommended which is usually not above 125° F. (52° C.).*

4. In the case of desiccated chemicals like sodium carbonate and sodium sulphite, *add the chemical to the water and not vice versa.*

Two practical methods of mixing are possible, as follows:

(a) Dissolve all the chemicals in one bottle or vessel by adding the solid chemicals to the water in the correct order (in the formula the ingredients should be named in the order in which they are dissolved). For example, to mix the following formula:

	Avoirdupois	Metric
Elon	45 grains	3.1 grams
Sodium Sulphite (E. K. Co.)	1½ ozs.	45.0 grams
Hydroquinone	135 grains	9.5 grams
Sodium Carbonate (E. K. Co.)	2½ ozs.	75.0 grams
Potassium Bromide	15 grains	1.1 grams
Water to make	32 ozs.	1.0 liter

proceed as follows:

Dissolve the Elon in 16 ozs. (500 cc.) of water (about 125° F.) (52° C.), then add the sulphite, and when completely dissolved, add the hydroquinone. Finally add the carbonate and bromide and cold water to make 32 ozs. (1 liter).

For large quantities the filter bag method should be used, the chemicals being placed in the bag and dissolved in the above order.

(b) An alternative method is to dissolve the preservative and developing agent in one vessel and the carbonate and bromide in another, cool and mix. This method is the safest and best for quantity production.

For example, to mix the following motion picture developer,

	Avoirdupois	Metric
Sodium Sulphite (E. K. Co.)	4 lbs.	1800.0 grams
Hydroquinone	13 ozs.	390.0 grams
Sodium Carbonate (E. K. Co.)	4 lbs.	1800.0 grams
Potassium Bromide	3 ozs.	90.0 grams
Water to make	10 gals.	40.0 liters

proceed as follows:

Dissolve the sulphite in about one gallon (4 liters) of water (125° F.) (52° C.), then dissolve the hydroquinone and

filter into the tank. Then add one gallon (4 liters) of cold water to the tank, dissolve the sodium carbonate and bromide in one gallon (4 liters) of hot water and filter this into the tank, immediately adding cold water up to ten gallons (40 liters). The object of adding cold water to the tank before adding the carbonate is to cool off the solution before the carbonate is added.

Mixing Concentrated Developers

The extent to which a developer may be concentrated is determined by the solubility of the least soluble constituent, because a stock solution should usually withstand cooling to 40° F. (4.4° C.) without any of the ingredients crystallizing out. (See Table of Solubilities, Page 99.) Usually, the hydroquinone and Elon come out of solution on cooling, but this may be prevented by adding wood alcohol or methanol in a concentration up to 10%. Denatured alcohol may be used if wood alcohol has been added as the denaturant. If a precipitate forms, however, on adding the denatured alcohol to the developer, the denatured alcohol is unfit for use.

The addition of the alcohol does not prevent the other ingredients such as sodium sulphite from crystallizing out, in fact, the alcohol diminishes their solubility and therefore increases the tendency to come out of solution.

A para-aminophenol-carbonate developer is difficult to prepare in concentrated form, though by adding a little caustic soda the solubility of the para-aminophenol is increased and a stronger solution can be thus prepared.

When preparing concentrated developers it is important to observe carefully the rules of mixing, taking care to keep the temperature of the solution as low as possible if a colorless developer is to be obtained.

The following formula is a typical example of a concentrated developer and is prepared by dissolving the ingredients in the order given:

	Avoirdupois	Metric
Water (about 125° F.) (52° C.)	16 ozs.	500.0 cc.
Elon	75 grains	5.3 grams
Sodium Sulphite (E. K. Co.)	2½ ozs.	75.0 grams
Hydroquinone	¾ oz.	22.5 grams
Sodium Carbonate (E. K. Co.)	3½ ozs.	105.0 grams
Potassium Bromide	38 grains	2.7 grams
Wood Alcohol	4¼ ozs.	136.0 cc.
Cold water to make	32 ozs.	1.0 liter

Two-Solution Developers

A two-solution developer is simply a one-solution developer split into two parts, one containing the carbonate and bromide, the other containing the developing agent and preservative so that the developer will oxidize less readily and therefore keep well. The reason why it is customary to keep a developer like pyro in two solutions, is because pyro oxidizes much more readily than Elon or para-aminophenol with a given amount of preservative.

For purposes of mixing only one-solution developers need be considered because the same rules regarding mixing apply in both cases.

How to Prepare Fixing Solutions

Fixing baths may be divided into the following classes:

1. *Plain hypo solutions.*
2. *Acid hypo solutions* consisting of hypo with the addition of sodium bisulphite, potassium metabisulphite, or sodium sulphite with acid.
3. *Acid hardening hypo solutions.*

1. No difficulty is usually experienced when mixing a *plain hypo solution*. When mixing a quantity of solution in a tank, the filter bag method (page 70) should be used and the hypo dissolved in warm water because the temperature drops considerably while the hypo is dissolving. If a scum forms on the surface of the solution on standing this should be removed by drawing the edge of a towel or blotter across the surface.

If a wooden cover is used for the tank, it should be waterproofed to prevent the formation of fungi which produce acid substances that turn the fixing bath milky. Waterproofing may be accomplished by dipping the cover several times in a nitrocellulose lacquer solution such as the Eastman No. 5119 Lacquer. The cover should be allowed to dry between each dipping; and it should be examined subsequently at intervals and redipped when necessary. An alternative method is to wax impregnate the wood by first thoroughly soaking the cover in water for several days to swell the pores and then immersing it in a suitable container holding hot paraffin wax. The wax should be kept hot during the treatment and any excess wiped off with a cloth. Wax impregnated covers have the disadvantage that they are quite heavy.

The slime which occasionally forms on the inner surface of wooden tanks can be removed by washing the tank out at intervals with sodium hypochlorite solution as described in the section on 'Cleaning Containers for Photographic Solutions,' page 97.

A plain fixing bath, however, is seldom used because it gradually becomes alkaline from an accumulation of alkali carried over by prints and films from the developer and this tends to soften the gelatin, while the image continues to develop in the fixing bath, so that if two prints stick together, more development takes place at the point of contact, causing uneven development. If the bath is acid, the acid kills or neutralizes the alkali in the developer carried over, thus preventing unevenness.

2. *All acid fixing baths* contain either sodium bisulphite, potassium metabisulphite, or a mixture of sodium sulphite and a weak acid, and the following directions for mixing should be followed:

a. Do not add the bisulphite or acid sulphite solutions to the warm hypo solution or the hypo will turn milky. The solutions should be quite cold when mixed.

b. On keeping, an acid hypo solution gradually becomes milky, so that a stock solution of the sodium bisulphite, etc., should be kept and added to the plain hypo stock solution as required. For general purposes $1\frac{1}{2}$ ozs. (45 cc.) of a 50% sodium bisulphite solution is added to 32 ozs. (1 liter) of a 35% hypo solution. If any considerable excess over this amount is added, the hypo rapidly turns milky especially in warm weather, owing to the liberation of sulphur.

A satisfactory bisulphite fixing bath has the following composition:

Bisulphite Fixing Bath

	Avoirdupois	Metric
Hypo	8 ounces	250.0 grams
Sodium Sulphite (E. K. Co.)	150 grains	10.5 grams
Sodium Bisulphite (E. K. Co.)	75 grains	5.3 grams
Water to make	32 ounces	1.0 liter

3. *Acid hardening fixing baths* are prepared by adding to hypo an acid hardening solution which contains the following ingredients:

a. An acid such as acetic, citric, tartaric, lactic, malic, maleic, sulphuric, etc., which stops development.

b. A hardening agent such as potassium alum, potassium chrome alum or formaldehyde, 40%.

c. A preservative such as sodium sulphite or sodium bisulphite. The latter acts as a preservative in two ways: It prevents the formation of sulphur by the action of the acid on the hypo, while it also prevents the developer carried over into the fixing bath from oxidizing and turning brown.

Prepare the acid hardening solution as a separate stock solution and add this to the hypo solution as required.

The order of mixing is important, as follows:

When mixing in one vessel, first dissolve the sulphite in warm water (about 125° F.) (52° C.), then add the acid and then the potassium alum. It is sometimes recommended to reverse the process, namely, dissolve the alum first, add the acid, and then the sulphite, but the alum dissolves more readily in the acid-sulphite solution.

Another method is to dissolve the alum and sulphite in separate solutions, cool, add the acid to the sulphite solution and then add the alum solution.

The hypo should be cool and dissolved completely before adding the cool hardener; otherwise sulphur is likely to be precipitated.

If the order of mixing is reversed and the alum added first to the sulphite a white sludge of aluminum sulphite is formed which dissolves with difficulty when the acid is added. Therefore, if after mixing, the hardener is milky and a sludge settles out it is due to a relative insufficiency of acid, that is, the acid used was either not up to strength or too much alum or sulphite was added.

With other hardening baths the order of mixing is usually the same.

Fixing baths containing chrome alum as the hardening agent usually have sulphuric acid as the active acid. (See Formula F-16, p. 56.) No difficulty should be found in mixing the bath providing care is taken in adding the sulphuric acid to the chrome alum solution. The acid should be poured slowly down the side of the mixing vessel while stirring the chrome alum solution to insure thorough mixing, since this acid is very heavy and will sink to the bottom if not mixed well. *Water should never be added to the sulphuric acid or the solution may boil and spatter some of the acid on the hands or face causing serious burns.*

Storage of Chemicals

Chemicals should be stored in well corked or well stoppered jars in a cool, dry place because most chemicals are affected by air, which contains oxygen, carbon dioxide gas and moisture.

(a) Oxygen readily attacks such substances as sodium sulphite, especially in the presence of moisture, converting it into sodium sulphate, which is useless as a preservative. With crystalized sodium sulphite the sodium sulphate forms on the outside of the crystals as a powder, which may be washed off and the crystals dried. It is not easy to detect sodium sulphate in desiccated sulphite except by chemical tests.

Other substances which combine with oxygen and are, therefore, said to be oxidized, are sodium bisulphite and potassium metabisulphite and all developing agents such as pyro, hydroquinone, etc., which turn more or less brown, the extent of the color roughly indicating the degree of oxidation.

(b) Carbon dioxide gas combines with substances like caustic soda and caustic potash, converting them into the corresponding carbonated alkalis which are less reactive. If sodium hydroxide is kept in a stoppered bottle the stopper usually becomes cemented fast by the sodium carbonate formed, so that it should be kept in a waxed corked bottle. Owing to the solvent action of the caustic alkalis on glass the inside of the glass bottle containing caustic or strongly carbonated solutions becomes frosted, though the quantity of glass thus dissolved away will usually do no harm.

(c) Certain chemicals have a strong attraction or affinity for the moisture in the atmosphere and gradually dissolve in the water thus absorbed, forming a solution. This phenomenon is termed "deliquescence" and the chemicals are said to be "deliquescent." Familiar examples are ammonium thiocyanate, potassium carbonate, sodium sulphide, uranyl nitrate, sodium bichromate, etc., which should be stored in corked bottles and the neck dipped in melted paraffin wax.

As mentioned earlier, it is difficult to prepare a solution of definite percentage strength from a chemical which has deliquesced, though it is usually sufficient to drain off the crystals, or to use a hydrometer, referring to a table giving the hydrometer readings in terms of percentage strength.

(d) While some chemicals absorb moisture as above, others give up their water of crystallization to the atmosphere, and therefore lose their crystalline shape and fall to a powder and are then said to "effloresce," the phenomenon being termed "efflorescence." Some crystals do not contain any water and therefore cannot effloresce.

A very dry atmosphere is suitable, therefore, for storing deliquescent salts but not for efflorescent salts. The only way to store chemicals is to isolate them from the air by suitably sealing.

(e) Some chemicals are decomposed by long exposure to light, especially sunlight. Such chemicals usually change more rapidly when made up as a solution than when stored in the solid form. Silver nitrate is probably the outstanding example. Crystals of this salt darken in light and a solution will darken quite rapidly. The remedy is to store both the solid and liquid in dark brown bottles. Potassium iodide solutions often turn a deep yellow color because of the liberation of free iodine. Nitric acid sometimes turns yellowish brown on standing in white bottles for long periods of time. Potassium ferricyanide solution turns blue on prolonged exposure to light owing to the formation of Prussian blue.

Stock solutions and developers should be stored in either hard glazed earthenware crocks, large glass bottles, wooden vats, or tanks of resistant material, and so arranged that the liquid may be drawn off at the side and near the bottom. (See section on "Apparatus," page 68.)

In case a solution such as Pyro has to be stored for a long time and withdrawn at intervals, an absorption bottle containing alkaline pyro may be fitted at the intake which absorbs oxygen from the air as it enters the bottle on withdrawing part of the solution.

Hard glazed earthenware crocks are most satisfactory for storage of stock solutions of developers and fixing baths for volumes of 5 gallons (20 liters) or more. The crocks should be fitted with waxed wooden covers. The method of attaching the outlet is important. If not supplied with a hole slightly above the base, the crock should be drilled. A right-angled lead tube should then be inserted through a rubber stopper and the tube and stopper fastened securely to the jar by passing a brass or monel metal band around it. A short length of pure gum rubber tubing may be fastened over the end of the lead tube and closed by means of a screw

clamp. Large glass bottles, although more susceptible to breakage, may also be used as containers, and these should be fitted in a similar way with either glass or lead tube outlets.

A battery of stock solution bottles or crocks may be arranged on lead covered shelves under which a large trough is placed, or, the floor may be so arranged as to form a sink so that in case of accidental breakage no serious damage is done. This precaution is of special importance in the case of hypo solutions, which might percolate into various rooms in a studio or laboratory and inoculate them with hypo dust, causing an epidemic of spots.

Wooden storage tanks may be reinforced against leaking by coating their inner surfaces with "Oxygenated Asphalt," as described under the section on "Apparatus," page 68.

CHAPTER X

Using Solutions

Photographic solutions, especially developers, vary considerably in their period of usefulness or time during which they may be utilized effectively to process exposed films and papers. This "useful life" as it is sometimes called, is, therefore, an important property of a solution and should be studied by everyone handling photographic materials. There are a good many factors which influence the useful life of a solution, such as whether it receives intermittent or continuous use, the extent of the surface exposed to the air, the temperature, the nature and reactions of the chemical constituents, and the manipulative procedure used in handling films or prints in the bath.

The average photographic solution is usually discarded as soon as its working rate is reduced to an impractical time period. Methods of reviving developers are somewhat vague and much work remains to be done on this subject. In the case of certain tank developers it is customary to add a replenisher solution several times before the developer is discarded. More is known about the revival of fixing baths however, but with these solutions it is usually safer and more economical except in specific cases to discard them after a certain period of usefulness than to bother with revival.

Conversely, some workers go to the other extreme and use solutions for several years merely by withdrawing a part of the used bath and adding fresh solution at regular intervals. Though this practice has some merit it is generally to be condemned since most photographic solutions accumulate certain reaction products that greatly reduce their efficiency and in addition may have harmful effects.

This chapter contains a summary of the characteristics of developers and fixing baths both with and without use, a discussion of troubles, the effect of temperature on solutions, and methods of cleaning containers for photographic solutions.

The Useful Life of Developers

Without Use. If a freshly mixed developer (prepared with water boiled to free it from dissolved air) is stored in a

completely filled and stoppered or wax-corked bottle, it will keep almost indefinitely even in the light. Under ordinary conditions of storage, the bottle or vessel contains more or less air. Also, when an ordinary cork or a non-airtight cover is used, the surface of the developer is continually in contact with air, the oxygen constituent of which oxidizes the developing agent and sodium sulphite present. This results in a lowering of the developing power in direct proportion to the amount of oxidation of the developing agent, which is accelerated as the preservative or sodium sulphite becomes oxidized also.

The oxidation products of developing agents are usually colored so that the developer on keeping frequently turns brown. In the presence of sodium sulphite, however, the oxidation products of hydroquinone consist of hydroquinone mono- and disodium sulphonates which are colorless. The fact that an old Elon-hydroquinone developer is colorless is, therefore, no indication that the original developing power is unimpaired. An oxidized Elon or Elon-hydroquinone developer also frequently fluoresces strongly.

In some cases when an Elon-hydroquinone developer gives slight developer fog when freshly mixed, the fogging tendency disappears on standing. This may be due to the anti-aerial fogging action of the developer oxidation products which are produced on keeping. (See paragraph on fog under "Developer Troubles," page 85.)

A solution of a developing agent, such as pyro, to be stored for a considerable time, will keep best in the presence of an acid sulphite such as sodium bisulphite rather than sodium sulphite which is slightly alkaline. It is always preferable therefore to prepare such a developer as two solutions: one containing the developing agent and sodium bisulphite, and the other the carbonate and bromide, and to mix these solutions as required for use. A plain solution of sodium sulphite oxidizes readily in contact with air at a concentration below 10%, but above this concentration it oxidizes very slowly. Stock solutions containing sodium sulphite alone or in combination with a developing agent should be prepared, so that the concentration of the sulphite is around 10% for maximum keeping properties. Owing to the relative insolubility of Elon in a sodium sulphite solution, it is not possible to prepare such stock solutions with Elon.

Sodium bisulphite keeps satisfactorily in more dilute solutions and is a better preservative than sulphite in the absence of carbonate. It is usual therefore to keep readily oxidizable developing agents such as pyro, amidol, etc., by mixing with sodium bisulphite. On adding sodium carbonate to sodium bisulphite, sodium sulphite and sodium bicarbonate are formed, so that in compounding a two-solution formula from a one-solution formula it is necessary to take care of this neutralization of the carbonate by using an extra quantity.

Single solution developers containing sodium hydroxide or potassium hydroxide do not keep unless well stoppered; pure gum rubber stoppers being most suitable.

With Use. During development, several reactions are taking place: (1) The developing agent and sulphite are being oxidized by the air; (2) the developing agent is being destroyed as a result of performing useful work in reducing the exposed silver halide emulsion to metallic silver; and (3) oxidation products of the developer and the by-products, sodium bromide and sodium iodide, are accumulating. The bromide and iodide and developer oxidation products restrain development while the oxidation products prevent aerial fog. The restraining action of the bromide and iodide is analogous to cutting down the exposure, so that with an old developer it is not possible even on prolonged development to get the ultimate result out of an under-exposure.

The time required to produce a definite contrast increases as a developer is used, and the solution ceases to be useful when the time required for this exceeds the maximum time which can be allotted for the developing operation. A deep tank developer, for example, is therefore discarded for one or more of the following reasons: (1) The time for complete development is excessively long; (2) The solution stains or fogs emulsions badly; and (3) The accumulation of by-products is so great that shadow detail is lost even with full development.

Developer Troubles

The Developer Gives Fog. Fog is the chief trouble caused by faulty mixing. It may be a result of violation of the rules of mixing such as dissolving the carbonate before the sulphite, mixing the solution too hot, omitting the bromide, adding too much carbonate or too little sulphite, the use of impure chemicals, etc.

With certain developers, notably those containing Elon and hydroquinone, a form of fog, known as aerial fog, is produced when film wet with developing solution is exposed to the air. Motion picture positive film developed on a reel is especially sensitive to aerial fog. It may be prevented by adding about 5% of old developer to the freshly mixed developer. This is more effective than increasing the concentration of bromide above the normal quantity added. The oxidized developer probably acts as an anti-fogging agent thus reducing the tendency for fog formation.

Negatives developed in a developer containing an excess of sulphite or one containing hypo or ammonia may show *dichroic* or *green fog*. This appears yellowish-green by reflected light, and a pink color by transmitted light. It is usually caused when the dissolved silver salts, under certain conditions, are reduced to metallic silver in a very fine state of subdivision, particularly in the shadow portions of the negative where no bromide is liberated during development. Fine grained emulsions are most susceptible to this form of fog. Information on prevention and removal of dichroic fog is given in an article "Stains on Negatives and Prints," obtainable from the Service Dept., Eastman Kodak Co., Rochester, N.Y.

Some deep tank developers may begin to fog a short time after they have been put into use. When this occurs it usually can be traced to the presence of sulphide in the solution caused by the action of bacteria which reduced the sulphite in the developer to sulphide. The fog may be cleared up by putting some waste film or plates through the solution or by adding a small quantity of lead acetate to the developer. The bacteria or fungi usually grow in the slimy deposit which accumulates on the inner walls of the tank. This deposit may be removed by sterilizing the container occasionally with bleaching powder. (See section on Cleaning Containers for Photographic Solutions, page 97).

The Solution is Colored. As a general rule, the developer when mixed should be colorless and if colored it should be suspected as being likely to give fog. In the case of a pyro developer mixed with bisulphite, which contains iron, an inky substance is formed as a combination product of the iron and the pyro, and this imparts a dirty bluish-red color to the solution although photographically it is harmless. If a two-solution pyro developer is mixed in dirty vessels

the B solution (which contains the carbonate and bromide) may be colored brown by the presence of a little pyro.

The Solution Does Not Develop. Omission of the developing agent or the carbonate may usually be suspected if a developer does not develop.

Precipitation of a White Sludge. If a white precipitate settles on standing, this is probably Elon. The precipitate may often be redissolved by adding 5% of wood alcohol or methanol, but if this is not successful, then the formula contains either too much Elon or sulphite or not enough carbonate. If it is known that the formula gives a clear solution when mixed correctly and should the Elon precipitate out during mixing when the sulphite is added, the precipitate will usually redissolve on adding the carbonate. If the final solution is not colored, no harm will have been done.

Scum. Scum may be picked up on films or plates from the surface of the developer especially if the solution has been allowed to stand unused for several days. The scum may consist of grease, solid matter, or developer oxidation products, especially if the developer contains pyro. The scum should be removed by passing the edge of a sheet of blotting paper along the surface of the solution or by using a skimmer, consisting of several layers of cheese cloth stretched over a square wire frame.

Miscellaneous Troubles. Various types of developer stains may be produced on films, plates, and papers. These are discussed in detail in the article referred to under "Fog," page 85. When a developer solution is not agitated sufficiently during the progress of development, characteristic markings are produced. This is occasionally observed with film developed on hangers or racks. These markings are usually the result of retardation of development along the sides of a hanger or rack caused by the accumulation of oxidized developer products and sodium bromide. They may be prevented by thorough agitation of the holder or rack during development.

The Importance of Rinsing

It is important to rinse films, plates and papers after development and before fixation. When a film or print is transferred from the developer directly to the fixing bath the alkali in the developer retained by the film or print neutralizes some of the acid of the fixing bath. The addition of developer

also gradually destroys the hardening properties of the fixing bath. Therefore, by removing as much developer as possible from the film or print by thoroughly rinsing in water or an acid rinse bath for 10 or 20 seconds, the life of the fixing bath is very much prolonged, while the tendency for stains and blisters to form is very much reduced.

Rinsing and Hardening Films or Plates. In warm weather it is only possible to rinse films or plates for one or two seconds; otherwise the gelatin will soften. If the chrome alum hardening bath (Formula SB-3, page 55) is used, rinsing in water may be omitted although a previous rinse for a few seconds in water will prolong the life of this bath also. *Films or plates should be agitated for several seconds after putting in the hardening bath; otherwise a chromium scum, which is difficult to remove is apt to form on the film.* This scum is composed of chromium hydroxide and is produced by the reaction between the chrome alum and the alkaline developer carried over on the film, but it does not form with a fresh bath if the film is well agitated on immersion. When the bath becomes old, a scum will tend to form even if the films are agitated; the bath should then be discarded. *Films should always be wiped with wetted cotton* after washing to remove any possible traces of scum, because once the film is dry it is impossible to remove it.

The hardening bath is a blue color by artificial light when freshly mixed, but it ultimately turns yellowish-green with use. *It then ceases to harden and should be replaced by a fresh bath.*

Rinsing Prints. Thorough rinsing will largely prevent staining troubles with prints and will allow a larger number to be fixed before the bath sludges. An acid rinse or "short stop" bath is strongly recommended instead of a water rinse because it arrests development immediately, whereas, when rinsing in water, development of the print continues if the rinsing is unduly prolonged.

When handling only a few prints, a rinse of 5 to 10 seconds is sufficient, but if large batches of prints are being processed, the rinsing time should be from 1 to 2 minutes. It is important to move the prints and see that they are separated while in the acetic acid rinse bath (Formula SB-1 page 55), and in the fixing bath to insure that the solutions have thorough access to all parts of every print. If prints are not rinsed, developer is carried over to the fixing bath and the alkali in the developer rapidly neutralizes the acid in the

fixing bath. When a certain quantity of developer has been carried over, a white sludge forms and the bath becomes alkaline. Prints fixed in an alkaline bath are likely to become stained brown. When an acid rinse bath is used, no harm is done if the prints are left in the rinse bath 10 or 20 minutes.

When an acid rinse bath is used, sludging of the fixing bath will never occur if the rinse bath is always kept acid. A simple method of testing whether the bath is alkaline or acid is to dip a strip of blue litmus paper in the bath. If the paper turns red, the bath is acid, but if it remains blue, the bath is alkaline.

The life of the acid rinse bath (Formula SB-1, page 55) used for papers is determined by the quantity of alkali carried over from the developer, which depends on the quantity of carbonate in the developer, the quantity of developer retained by the print, and the time of draining. With a 1- to 2-seconds drain and a typical Elon-hydroquinone developer, the equivalent of approximately seventy-five 8x10 prints per gallon (forty $3\frac{1}{4} \times 5\frac{1}{2}$ prints per pint) may be processed safely in the acid rinse bath before the bath becomes alkaline.

The Properties of Fixing Baths

A plain solution of hypo is seldom used as a fixing bath but it is usually used in conjunction with a weakly acid salt such as sodium bisulphite, or more commonly with an acid hardening solution. The standard hardener contains a preservative, sodium sulphite, which prevents decomposition of the hypo; an acid, usually acetic acid, to neutralize any alkali carried over in the film from the developer and thereby arrest development; and a hardening agent, either potassium alum or chromium alum.

A satisfactory acid hardening fixing bath should have certain properties, namely, a fairly rapid rate of fixation, good hardening, a long sludging life, and a long "useful" life. The time for fixation is usually taken as twice the time for the milkiness or opalescence of the unreduced silver salts to disappear. This depends on the strength of the hypo (30% to 40% fixes most rapidly), the photographic material tested (portrait films fix in about 3 to 5 minutes whereas lantern slides clear in 30 seconds to 1 minute), the temperature of the solution (65° F. or 18° C. is recommended), and the degree of exhaustion of the solution.

The hardening properties are influenced by a large number of factors. A certain minimum quantity of alum is required to give the necessary hardening, while an excess of alum may produce too much hardening and induce brittleness. Normal fixing baths such as Formula F-1, page 55, are compounded carefully to give a hardening of 130° to 170° F. (54° to 77° C.). This is determined by immersing a strip of the fixed and washed films in water and heating the water slowly until the gelatin flows away from the support. For maximum hardening using a 5-seconds rinse in water between development and fixation, and washing one hour in running water after fixation, films should be fixed 15 to 20 minutes in either fresh or partially exhausted fixing baths.

A fresh chrome alum fixing bath loses its hardening properties rapidly whether it is in use or not. For this reason a potash alum fixing bath is usually to be preferred for long periods of usage.

A good fixing bath should not sludge during its useful life when used at 65° to 70° F. (18° to 21° C.). Changes in temperature of the fixing bath affect the rate of fixation and the useful life of the solution. For example, if a film requires 95 seconds to clear at 65° F. (18° C.), it would take about 60 seconds to clear at 85° F. (29° C.), but it is dangerous practice to allow the temperature of the bath to rise above 70° F. (21° C.) as the solution is apt to precipitate sulphur.

Under tropical conditions where high temperatures prevail, it is obviously often impossible to keep the temperature within this limit, and the fixing bath must usually be replaced oftener. A different technic must therefore, be used for tropical processing, where the secret lies in preventing abnormal swelling of the gelatin, for once it is swollen it is almost impossible to reduce it and to handle the film. For more complete information on this subject, the booklet "Tropical Development" should be consulted. This is obtainable on request from the Service Dept., Eastman Kodak Company, Rochester, N. Y.

The Useful Life of Fixing Baths

A fixing bath in use becomes exhausted as a result of performing useful work in fixing out the emulsion. The acidity of the bath is being reduced by the developer carried in, although at first this tends to favor a longer "sulphurization life" or period of time before the bath precipitates sulphur.

With use, however, the solution finally reaches a point where a sludge of aluminum sulphite is precipitated, rendering the bath useless. During the first stages of use, the hardening properties increase slightly, after which they fall off rapidly. A fixing bath is usually exhausted if it froths at the surface, or if it becomes milky or sludges throughout the solution. The bath may also fix so slowly that there is danger of removing the films or prints before they are completely fixed. When the time of clearing for a slow fixing film exceeds 12 to 15 minutes, the bath should be discarded.

The F-1 and the F-16 fixing baths on pages 55 and 56 will fix completely the equivalent of seventy-five 8 x 10 films or plates, and the F-1 formula, one hundred 8 x 10 prints per gallon, provided a thorough water rinse precedes fixation. If a 2- or 3-minute immersion in a suitable hardening bath (Formula SB-3 page 55) is given between development and fixation, the equivalent of one hundred 8 x 10 films may be fixed per gallon.

When making prints, if the acid rinse bath (Formula SB-1, page 55) is used between development and fixation, the fixing bath will not sludge so rapidly and the equivalent of one hundred and twenty-five 8 x 10 prints may be fixed safely per gallon of Formula F-1.

These figures have been established by careful tests and it is recommended that the fixing bath be discarded and replaced by a fresh bath when approximately this number of films or prints have been fixed.

Recovery of Silver from Exhausted Fixing Baths

An exhausted fixing bath contains dissolved silver salts and various methods may be employed to recover the silver profitably, providing at least 5 gallons of well exhausted hypo are discarded each week. For large volumes of exhausted baths (about 100 gallons or more per week) precipitation with sodium sulphide is the most economical and rapid method. Precipitation with zinc dust is efficient when smaller volumes of bath are to be treated, and has the advantage that no objectionable fumes of hydrogen sulphide are evolved, as in the sulphide process.

Recovery by means of commercial electrolytic units also represents a simple and economical procedure for volumes of exhausted baths of less than 100 gallons per week. Electrolytic units give best results when used in a discarded fixing bath, rather than in a working bath.

Although it is possible for a capable chemist, to so restore a fixing bath by desilvering, subsequently clarifying, and modifying its composition, that its useful life is prolonged, it is just as economical and preferable to prepare a fresh bath.

Working details of the various methods of silver recovery and a discussion of the economics of the processes are given in a paper on silver recovery obtainable on request from the Service Dept., Eastman Kodak Company, Rochester, N. Y.

Fixing Bath Troubles

A. *Sludging of the Fixing Bath*: A fixing bath occasionally turns milky soon after the hardener is added, and sometimes after being in use for a short time. The milkiess may be of two kinds:

1. If the precipitate is *pale yellow* and settles very slowly on standing, it consists of sulphur and may be caused by (a) too much acid in the hardener; (b) too little sulphite or the use of impure sulphite, in which case there is not sufficient present to protect the hypo from the acid; (c) high temperature. The hardener should only be added to the hypo solution when at room temperature. If the temperature of the acid fixing bath is over 85° F. (29° C.), it will not remain clear longer than a few days even when mixed correctly. The only remedy is to throw the bath away and mix fresh solution as required.

If a sulphurized bath is used, the sulphur is apt to penetrate the gelatin, and later may cause fading of the image.

2. If the precipitate is *white*, and a gelatinous sludge of aluminum sulphite settles on standing, it may be caused by (a) too little acid in the hardener; for example, supposing a formula calls for pure glacial acetic acid and 28% acid is used by mistake, then less than one-third the required concentration of acid is present; (b) too little hardener in the fixing bath. When fixing prints, a relatively large proportion of the developer is carried over to the fixing bath (unless a water or acid rinse bath has been used) which soon neutralizes the acid, and therefore increases the tendency for precipitation of aluminum sulphite. In the same way a fixing bath with the correct proportion of hardener, when exhausted, still contains alum and sulphite but no acid, and these combine to form a sludge of aluminum sulphite.

It is extremely important, to use only the acid specified and to know its strength, *because trouble is caused if more or*

less acid is used than is called for in the formula. It has been found that the hardening properties of an alum-acid fixing bath bear a relation to the tendency of the bath to precipitate aluminum sulphite. In other words, a bath containing an excess of acid (and which therefore may be used for a relatively long time before the aluminum sulphite precipitates), does not harden as well as a bath which precipitates when a much smaller volume of developer is added. With such a bath containing a minimum of acid it is advisable to add a further quantity of acid as soon as a slight precipitate appears; a satisfactory quantity being about one-half that originally present in the bath.

B. *The bath does not harden satisfactorily.* Insufficient hardening may be a result of (1) the use of inferior alum which does not contain the correct proportion of aluminum sulphate; (2) the presence of too much acid or sulphite; or (3) an insufficient quantity of alum. On varying the proportions of acid, alum and sulphite in a fixing bath, it has been found that the hardening increases as the quantity of alum increases. With increasing quantities of acetic acid, with a given quantity of alum, the hardening increases to a maximum, beyond which it decreases until the solution does not harden at all. A certain minimum quantity of acetic acid, however, is necessary to give the fixing bath a fairly long, useful life, before aluminum sulphite precipitates, but this quantity is usually greater than the quantity which produces maximum hardening. With use, therefore, the hardening ability of most fixing baths at first increases with the addition of developer to a maximum, beyond which the hardening falls off rapidly.

C. *Blisters.* When the sodium carbonate of the developer is neutralized by the acid in the fixing bath, carbon dioxide gas is evolved which produces blisters if the gelatin is too soft to withstand the disruptive action of the gas. If the fixing bath contains an excess of acid and the films are not rinsed sufficiently, or if a strongly acid rinse bath is used, blisters are apt to be formed. On dry film, blisters appear as tiny crater-like depressions when examined by reflected light. This trouble is more liable to occur in hot weather, and especially when the bath is not hardening sufficiently.

D. *Dichroic Fog.* If the fixing bath does not contain acid or if it is old and exhausted and contains an excess of dissolved silver salts, a stain called *dichroic fog* is sometimes produced on the film. In reflected light, film stained in this

way appears yellowish-green and by transmitted light it looks reddish-pink. Dichroic fog never occurs in a fresh acid fixing bath, or if the film is rinsed before fixing and the temperature of the bath is kept at 65° to 70° F. (18° to 21° C.). Methods of removal of dichroic fog are discussed in the booklet, "Stains on Negatives and Prints" obtainable from the Service Dept., Eastman Kodak Company, Rochester, N. Y.

E. *Scum on Fixing Baths.* When a partially exhausted fixing bath is allowed to stand several days without use, the hydrogen sulphide gas usually present in the air reacts with the silver thiosulphate in the bath and forms a metallic appearing scum on the surface of the solution. This scum consists of silver sulphide and should be removed by drawing the edge of a sheet of blotting paper across the surface of the bath, or by using a skimmer made of several strips of cheesecloth stretched over a wire frame.

A white scum consisting of aluminum sulphite is found sometimes on films or prints. This is caused by: (1) insufficient rinsing after development; (2) too low a concentration of acid in the fixing bath; (3) insufficient agitation of the film on first immersing in the fixing bath. Since aluminum sulphite is soluble in alkali, the scum may be removed by swabbing the film or print with a 10% solution of sodium carbonate and then washing thoroughly.

With chrome alum fixing baths, a scum composed of chromium hydroxide is produced as described under the section on "The Importance of Rinsing," page 87. Films which are fixed in such a bath should always be wiped carefully with wetted cotton for if any chromium scum dries on the surface it is impossible to remove it. A chrome alum fixing bath is not recommended for use with papers because of its slight staining characteristics.

F. *Stains.* Several different types of stains such as white aluminum sulphite stain (see E above), sulphur stains, and yellow silver stains, are occasionally produced. For a complete discussion of fixing bath stains reference should be made to the article on this subject obtainable from the Service Department, Eastman Kodak Company, Rochester, N. Y.

G. *Mottle.* When processing film or plates in hangers, a mottled image is occasionally found when the hanger has not been agitated enough on first immersing in the fixing bath, or if the film is insufficiently rinsed between development and fixation. In the absence of thorough rinsing and agitation, development continues locally during the first few minutes

of fixing and in these spots the image has greater density. Mottle is also produced if the ends of the hanger protrude above the surface of the fixing bath, especially during the first stages of fixation.

Effect of Temperature on Chemicals and Solutions

Nearly all chemicals used in photographic work have a high enough melting point so that there is little danger of the solids melting while stored in bottles or other containers, but it is good practice to keep storage bottles as dry and cool as possible. Bottles or cans, for instance, should not be placed on shelves or in cupboards near a stove or where direct sunlight can shine upon them.

When in solution the effect of temperature on chemicals is much greater and must be taken into account with every photographic solution. Under normal working conditions, a temperature of 65° F. (18° C.) is recommended for negative development, and 70° F. (21° C.) for print development.

Temperatures of solutions are measured either by the Centigrade or Fahrenheit thermometer. On the Centigrade thermometer water freezes at zero and boils at 100 degrees, and on the Fahrenheit scale the corresponding readings are 32 degrees and 212 degrees, so that 100 degrees C. are equivalent to 212 degrees minus 32 degrees or 180 degrees F., that is, 1 degree C. is equivalent to $\frac{9}{5}$ degrees F.

To convert degrees Centigrade to Fahrenheit, multiply by $\frac{9}{5}$ and add 32. To convert degrees Fahrenheit to Centigrade subtract 32 and divide by $\frac{9}{5}$.

Most chemical reactions proceed more rapidly as the temperature is increased, and this is true of all the reactions involved in photography, so that developers and fixing baths will act much more rapidly when warm than when cold. Different reactions are stimulated to different extents by rise of temperature, and the effect of temperature can be measured numerically, the result obtained being termed the "temperature coefficient" of the reaction.

As a general rule, the temperature coefficient is measured for a change of temperature of 10 degrees Centigrade, equivalent to 18 degrees Fahrenheit. Therefore, if a reaction takes 4 minutes at 60° F. (15° C.) and is completed in 2 minutes at 78° F. (25° C.) it is said to have a temperature coefficient of 2, the rate of reaction being doubled for a rise of 18° F. (10° C.).

The temperature coefficient of development varies with the developing agent, being least with the developers of high reduction potential, such as Elon, and most with developers of low reduction potential, such as hydroquinone. There is one consequence of this which is rather important, namely, that the behavior of a mixed hydroquinone developer depends upon the temperature. At low temperature the hydroquinone is very inert, while the Elon is not decreased in its rate of action to the same extent, and consequently the developer behaves as if it contained an excess of Elon. At high temperatures the hydroquinone is increased in its activity far more than the Elon, and the situation is reversed.

A similar principle applies to the fogging produced by developers. If development is continued for a sufficient time all developers will fog, but the fog reaction is a different one to that of development, and apparently has a different temperature coefficient and one which is much higher than the temperature coefficient of the development reaction itself. Consequently, a developer which will develop a material to a good density with low fog at a normal temperature, may produce very bad fog if the temperature is high.

From the above it will be understood that the control of temperature in photography is of great importance and that so far as possible development and fixation should always be carried out at a normal temperature (65° to 70° F.) (18° to 21° C.), a serious change in temperature involving much greater care and the risk of difficulty. If the temperature is too high, then trouble may be encountered with fog and with softening and frilling of the material, while if the temperature is too low, development will be delayed, there is danger of under-development, and fixing will be slow so that the greatest care must be taken to insure thorough fixation.

Fixing baths frequently decompose very rapidly with liberation of free sulphur if kept for a few hours to a few days at temperatures over 95° F. (35° C.). Although the rate of fixation is increased at higher temperatures, it is very bad practice to allow the temperature of a fixing bath to rise above 75° F. (24° C.); the recommended temperature being 65° F. (18° C.). In storing large volumes of fixing bath it is best to store the hypo and hardener solutions separately and add the cool hardener to the cool hypo when the latter is put into a working tank.

Some strongly oxidizing solutions, acid permanganate, in particular, when employed at high temperatures rapidly

lose their effectiveness for photographic use owing to secondary reactions. Usually these solutions work best at temperatures below 70° F. (21° C.).

Some photographic solutions, notably a hypo alum toning bath, are recommended to be used at 120° to 130° F. (49° to 54° C.), but even these solutions should be watched carefully to see that the temperature does not rise above that recommended, otherwise blistering, staining, and degradation of tone will result.

About the best general rule for temperature is to mix, store, and use the solutions at the temperature recommended in the manufacturer's instructions.

When the temperature cannot be controlled, as may be the case in the tropics, special measures must be taken as described completely in the booklet, "Tropical Development" obtainable on request from the Service Department, Eastman Kodak Company, Rochester, N. Y.

Cleaning Containers for Photographic Solutions

Apparatus used for mixing and containing photographic chemicals become discolored and sometimes coated with decomposition products of the solution. In certain cases this does no harm, especially if the container is always used for the same kind of solution, but it is much better technic to clean all containers each time they are emptied. With cheaper containers, such as bottles and old trays, it is not worth wasting time if these are difficult to clean. It is better to discard the container and use a new one.

Most cleaning solutions are either strong alkalis or acids, and should be used with the same discretion given these chemicals when mixing photographic solutions. The principle of a cleaning solution is that it acts on the stain or deposit and changes it to a soluble form, which dissolves in the cleaning agent, or may be washed out with water. Sometimes the cleaning agent merely softens the deposit sufficiently so that it may be removed by the use of a wire brush or an abrading substance like sand or glass beads.

The most common tray cleaner is an acid solution of potassium bichromate made by dissolving 3 ounces (90 grams) of potassium bichromate in 32 ounces (1 liter) of water, and adding slowly with stirring, 3¼ ounces (100 cc.) of concentrated sulphuric acid. This solution will remove stains,

caused by oxidation products of developers, silver stains, and some dye stains, and is a very useful cleaning agent.

Other solutions which will be found useful are 1% permanganate, (followed by treatment in 50% bisulphite to remove the residual brown manganese stain); 40% sodium hydroxide (caustic soda); and any of the strong mineral acids, such as sulphuric, hydrochloric, and nitric. After removal of the stain, the vessel should be washed thoroughly to insure complete removal of the cleaning agent.

When an acid fixing bath sulphurizes, the colloidal sulphur is quite difficult to remove with a cleaning agent, but the addition of glass beads or sand to the bottle or other vessel with shaking will be found effective. A hot, concentrated solution of sodium sulphite (about 20%) will also usually dissolve sulphur.

Enamelled trays or tanks which have been used with strongly alkaline developers or caustic solutions, rapidly lose their glossy surface and become roughened and discolor easily. If such containers are used with dye solutions, the dye is taken up in the pores of the enamel, and it is a very difficult matter to remove it completely. Trays badly discolored in this way are not worth the time to clean them.

Large tanks of wood, Alberene, or stoneware, after several weeks of use as developer containers, become coated with a layer of slime or mold which should be cleaned out by thoroughly scrubbing the walls with a wire brush, and then treating with sodium hypochlorite solution. The solution should be added in the following proportion: 1 part of 10% hypochlorite solution to 6 parts of water. After the solution has been left in the tank overnight it should be emptied out and the tank given another thorough scrubbing and several washings previous to being put into service again. A stock solution of hypochlorite is prepared by making up a 4% solution of calcium hypochlorite and converting this into sodium hypochlorite. To prepare this solution, sodium carbonate solution (10%) is added to the calcium hypochlorite solution until no more precipitate forms, and the solution is then allowed to stand until all the precipitate settles to the bottom of the container. The remaining liquid is then drawn off for use as a stock solution.

Table of Chemical Solubilities

The following table will serve as a guide when preparing stock solutions of photographic chemicals. Since a solution is apt to become cooled in winter to a temperature approximating 40° F., it is not advisable to prepare a stock solution stronger than is indicated by the solubility of the chemical at this temperature.

Substance	Ounces of chemical in 100 ozs. (fluid) of Saturated Solution at	
	40° F. (4.4° C.)	70° F. (21.1° C.)
Acid, Acetic (any strength)	Mixes in all proportions	
Acid, Citric	78	88
Acid, Oxalic	7¼	14½
Acid, Tartaric (dextro)	73	78
Acrol or Amidol (See Diaminophenol Hydrochloride)	Mixes in all proportions	
Alum, Ammonium	6¼	15½
Alum, Iron	48	59
Alum, Potassium	6¼	11½
Alum, Potassium Chrome	15½	20½
Amidol or Acrol (See Diaminophenol Hydrochloride)	Mixes in all proportions	
Ammonia Solution	Mixes in all proportions	
Ammonium Bromide	52	57
Ammonium Carbonate	26	31
Ammonium Chloride	26	30
Ammonium Iodide	104	109
Ammonium Oxalate	2¾	5¼
Ammonium Persulphate	52	62
Ammonium Thiocyanate or Ammonium Sulphocyanide	62	73
Ammonium Thiosulphate, anhydrous	83	88
Borax (Sodium Tetraborate)	2½	7¼
Caustic Potash (See Potassium Hydroxide)	Mixes in all proportions	
Caustic Soda (See Sodium Hydroxide)	Mixes in all proportions	
Copper Sulphate, crystal	26	31
Diaminophenol Hydrochloride (Acrol or Amidol)	20½	26
Elon (Monomethyl para-amino phenol sulphate)	5¼	8¼
Ferrous Sulphate	29	41
Formalin	Mixes in all proportions	
Hydroquinone	4¼	6¾
Hypo (See Sodium Thiosulphate)	Mixes in all proportions	
Kodolon (See Para-aminophenol oxalate)	Mixes in all proportions	
Lead Acetate	31	47
Lead Nitrate	39½	51
Mercuric Chloride	4	6¼
Para-aminophenol oxalate (Kodolon)	1¼	2½
Potassium Bichromate	6¾	14½
Potassium Bromide	50	56
Potassium Carbonate, anhydrous	83	85
Potassium Chloride	26	31

Substance	Ounces of chemical in 100 ozs. (fluid) of Saturated Solution at	
	40° F. (4.4° C.)	70° F. (21.1° C.)
Potassium Citrate	93	104
Potassium Cyanide	46	52
Potassium Ferricyanide	30	36
Potassium Ferrocyanide	17½	26
Potassium Hydroxide (Caustic Potash)	78	83
Potassium Iodide	99	104
Potassium Metabisulphite	47	57
Potassium Oxalate	29	36½
Potassium Permanganate	3¼	6¾
Pyrogallol (Pyro)	36	57
Silver Nitrate	109	135
Sodium Acetate, anhydrous	31	36
Sodium Acetate, crystal (trihydrate)	52	62
Sodium Bicarbonate	7¼	9¼
Sodium Bisulphite	52	52
Sodium Bromide	67	73
Sodium Carbonate, anhydrous	10¼	24
Sodium Carbonate, crystal	29	65
Sodium Chloride	31	31
Sodium Hydroxide (Caustic Soda)	50	83
Sodium Phosphate, dibasic crystal	6½	24
Sodium Sulphate, anhydrous	5¼	20½
Sodium Sulphate, crystal	10¼	41
Sodium Sulphide, fused	13½	17¾
Sodium Sulphide, crystal	36¼	47
Sodium Sulphite, anhydrous	17½	28
Sodium Tetraborate (See Borax)		
Sodium Thiosulphate, (Hypo) crystal	73	93
Uranyl (Uranium) Nitrate	114	130

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